

PLANT LEAVES AS A BIOGEOCHEMICAL INDICATOR OF THE ENVIRONMENTAL STATE IN DIFFERENT REGIONS OF AZERBAIJAN

Roza Mammadova Nazim¹, Shalala Salimova Jafar²,
Sultan Huseynova Maharram³, Gunay Mammadova Israphil^{3,4},
Turkan Hasanova Allahverdi^{5✉}, Hijran Rafiyeva Latif⁶,
Gunel Jafarova Ali³

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Abstract

Urban ecosystems in Azerbaijan are increasingly affected by environmental pollution, making the application of biogeochemical methods essential for assessment and monitoring. In this study, leaves of dominant tree and shrub species were collected from six cities representing different functional zones (industrial, transport, residential, and recreational) during the main growing season (August-September). Samples were analyzed for ash content and elemental composition using atomic absorption, atomic emission, and mass spectrometric methods. The findings show that urban plants accumulate Zn, Cu, Cd, and Pb at levels exceeding background values, with the highest enrichment observed in industrial and transport zones. Species-specific differences in accumulation capacity were identified, allowing certain plants (e.g., *Betula pendula*, *Acer negundo*, *Populus* spp.) to be recommended as reliable biogeochemical indicators and as suitable material for urban greening.

Key words: heavy metals, biogeoindication, pollution, ash content, leaves

Introduction. The modern process of urbanization and several environmental problems associated with it necessitate the indication and objective assessment of the urban environment state. Among the monitoring methods, an

important place is occupied by the recording of pollutants content in living organisms, a response that has biological significance. Plant leaves are informative indicators about the state of the urban environment. The leaf blade functions as a powerful air pump for plants and helps absorb and accumulate pollutants originating from industrial emissions. The relevance of the work is due to the need to implement biogeochemically significant methods for monitoring of environmental pollution. The high level of anthropogenic load determines the need to apply objective methods for assessing the current and future development of the environmental situation. Leaves of different plant species are characterized by specificity in accumulation of heavy metals. Various plant species and their parts are used as biogeochemical indicators of pollution, particularly heavy metals. The mechanism of ion absorption by a leaf is a multi-stage process, involving both passive diffusion and active transport. The main phases of pollutant uptake and accumulation are sorption by the cuticular layer and epidermal cells, then diffusion through stomatal slits in the leaf, dissolution in water saturating the leaf membranes, and finally movement from the site of absorption to connective tissues and accumulation inside the cells [1, 2]. This study aims to evaluate environmental pollution in Azerbaijani cities through the biogeochemical response of tree and shrub leaves, with a focus on identifying species with high accumulation capacity, determining regional background concentrations, and assessing their potential as bioindicators for urban ecosystems [3]. Based on the obtained data, species of tree and shrub plants were identified, whose leaves can be used to diagnose pollution in urban ecosystems caused by heavy metals. A significant result of the work is the determination of conditionally background concentrations of elements for the studied region. Certain plant species can be recommended as biogeochemical indicators of the state of the urban environment and as material for urban greening.

Methods. Six regions of Azerbaijan – Baku (40.42°07'93"N, 49.83°75'42"E), Ganja (40.64°36'21"N, 46.37°27'66"E), Nakhchivan (39.19°00'14"N, 45.39°83'81"E), Barda (40°48'25"N, 47°23'53"E), Lankaran (38°45'13"N, 48°51'04"E), and Sumgayit (40°73'66"N 49°65'26"E) – which differ in economic (number of residents, amount of cars and large enterprises) and geographical (relief, climate, etc.) conditions were studied. The objects of the study were the leaves of dominant species of woody and shrubby plants – 14 species of woody and 3 species of shrubby vegetation. The following plant species were studied: *Acer negundo* L., *Betula pendula* Roth., *Salix alba* L., *Populus alba* L., *Populus nigra* L., *Populus tremula* L., *Malus silvestris* Mill., *Sorbus aucuparia* L., *Fraxinus excelsior* L., *Ulmus glabra* L., *Ulmus minor* L., *Ulmus laevis* Pall., *Rosa canina* L., *Elaeagnus argentea* Pursch., *Crataegus oxyacantha* L., *Syringa vulgaris* L., *Quercus iberica*, and others. In each region more than 10 sites were laid out, which were zoned depending on the anthropogenic load and functionality: recreational (squares, parks), residential, transport (along major highways) and

industrial zones (near operating industrial enterprises) [4,5]. Dominant species of trees and shrubs were collected at each site. Species represented by single samples were taken into account. Standard methods were used for selection, transportation, storage and preparation of plant samples. Leaf samples were taken using the average sample method: at a height of 1.5–2.0 m from the ground surface for trees and 0.5–1.0 m for shrubs from the outer side of the crown along the circumference. To identify the accumulative capacity of plant leaves in urban conditions, they were taken during the main growing season (August–September). Plants of the same age were selected for sampling whenever possible. Leaves were taken for analysis without petioles. In the laboratory, plant leaf samples were thoroughly washed with distilled water to remove dust and soil particles, after which they were brought to an air-dry state. The background sites for each city were located 50–80 km from the city, on the opposite side from the wind rose, which minimized the impact of industrial emissions. To determine the concentration of chemical elements in plant leaves, wet decomposition of samples was performed [6,7]. A dry plant sample weighing 0.5000 ± 0.0001 g was decomposed by autoclaving with the addition of concentrated HNO_3 and H_2O_2 for 4 hours at $160 \pm 5^\circ\text{C}$. The determination of element concentrations was carried out using a SOLAAR M6 series atomic absorption device, an iCap-6300 atomic emission spectrometer, and an Elan 9000 mass spectrometer. Multi-element standard solutions registered in the State Standards Register of the Azerbaijan Republic were used to construct calibration graphs. The quality control of analytical work was carried out by measuring the calibration solution every 10 samples. If the calibration results were unsatisfactory (a deviation of 8–10% in the calibration graph), the device was recalibrated, taking into account the new background parameters.

Elements with concentrations below the detection limit, as well as those whose content did not meet the control criteria with respect to internal and external standards and interlaboratory comparison, were not considered. Ash content in plant leaves was determined using the generally accepted method. The obtained results were statistically processed using the STATISTICA and Microsoft Excel programs. The accumulation of chemical elements in the leaves of trees and shrubs in urban conditions was assessed using the concentration coefficient (C_C), which is the ratio of the element content in the leaves of plants to its concentration in the leaves growing in background areas [8,9].

Results. The elements whose contents in the leaves of trees and shrubs exceed background values were evaluated [10]. The average content of elements in the leaves of trees and shrubs in the studied regions of Azerbaijan (industrial, transport, residential, recreational) were determined. All the studied cities are characterized by the accumulation of Cd and Pb by plant leaves, as well as Li, Ni and U for Sumgayit, Cr and Cu in Barda, and Cu and Ni in Nakhcivan. The main attention was paid to the studying indicator properties of the leaves of woody and shrubby plants with respect to heavy metals such as Zn, Cu, Cd and Pb. These

elements are considered priority pollutants in soils and other natural environments of all the studied cities. Cd and Pb are toxic and belong to the first hazard class. Heavy metal pollution turns out to be less toxic to human health in the determined regions.

According to numerous toxicological studies, even in small concentrations, they can lead to various pathologies of living organisms, while an excess zinc and copper can cause a deficiency (inhibition) of other important micro and macro components (such as enzymes) in the body [11,12]. For Cd and Zn, a noticeable excess over the average content in soil vegetation was revealed 10 and 1.5 times, respectively, in Sumgayit indicators were exceeded by 54 and 4 times. According to the classification used, the average content of the studied elements in the leaves of the plants falls within the range of sufficient or normal concentration [9]. The exception is the level of zinc concentration in the leaves of woody and shrubby vegetation of Sumgayit city, where this element was found in excess (toxic) concentration. The variability of toxic metal content in the leaves of trees and shrubs

T a b l e 1
(a) Content of heavy metals (mg/kg) and ash (%) in the leaves

Region	Zn	Cu	Cd	Pb	Ash content %
Baku (<i>n</i> = 123)	$\underline{56.7 \pm 3.2}$ 5.7–147.7 (13.1)	$\underline{4.4 \pm 0.24}$ 0.56–13.1 (1.1)	$\underline{0.34 \pm 0.02}$ 0.04–1.3 (0.05)	$\underline{1.1 \pm 0.07}$ 0.09–5.5 (0.13)	$\underline{10.4 \pm 0.22}$ 5.9–14.3 (7.9)
Ganja (<i>n</i> = 131)	$\underline{44.9 \pm 3.0}$ 7.1–141.6 (12.2)	$\underline{3.9 \pm 0.19}$ 0.50–10.5 (0.78)	$\underline{0.12 \pm 0.008}$ 0.01–0.50 (0.03)	$\underline{1.1 \pm 0.10}$ 0.10–6.3 (0.16)	$\underline{10.5 \pm 0.17}$ 6.3–14.7 (7.6)
Barda (<i>n</i> = 147)	$\underline{31.0 \pm 1.8}$ 6.2–127.2 (9.1)	$\underline{4.1 \pm 0.18}$ 0.65–9.5 (0.75)	$\underline{0.13 \pm 0.014}$ 0.01–0.66 (0.03)	$\underline{1.6 \pm 0.11}$ 0.20–7.3 (0.21)	$\underline{8.9 \pm 0.19}$ 5.0–14.3 (6.6)
Lankaran (<i>n</i> = 148)	$\underline{35.9 \pm 2.3}$ 7.5–160.8 (11.7)	$\underline{4.5 \pm 0.27}$ 0.69–19.6 (0.91)	$\underline{0.22 \pm 0.02}$ 0.01–1.9 (0.04)	$\underline{0.52 \pm 0.04}$ 0.07–2.6 (0.08)	$\underline{9.6 \pm 0.20}$ 5.0–17.0 (7.4)
Nakhcivan (<i>n</i> = 116)	$\underline{45.2 \pm 3.1}$ 9.2–190.6 (12.2)	$\underline{4.6 \pm 0.27}$ 0.70–21.8 (0.78)	$\underline{0.11 \pm 0.007}$ 0.01–0.40 (0.03)	$\underline{0.98 \pm 0.08}$ 0.07–4.4 (0.16)	$\underline{9.5 \pm 0.16}$ 6.0–12.4 (7.6)
Sumgayit (<i>n</i> = 158)	$\underline{120.9 \pm 12.4}$ 9.4–923.6 (17.1)	$\underline{10.1 \pm 0.89}$ 0.8–65.1 (1.6)	$\underline{1.9 \pm 0.27}$ 0.11–21.0 (0.17)	$\underline{15.0 \pm 1.3}$ 0.36–90.1 (0.66)	$\underline{9.9 \pm 0.21}$ 5.6–16.5 (8.0)
Concentration of heavy metals in leaves: adequate/ overabundant [9]	$\underline{27-150}$ 100–400	$\underline{5-30}$ 20–100	$\underline{0.05-0.2}$ 5–30	$\underline{5-10}$ 30–300	–

Note: *n* – number of samples; first row – mean ± SE; second row ± range; (%) background value; SE – standard error

(b) Content of heavy metals (mg/kg dry weight) and ash content (%) of leaves by plant species

Plant species	<i>n</i>	Zn	Cu	Cd	Pb	Ash content
<i>P. nigra</i> L.	73	$\frac{86.6 \pm 4.3}{4.4}$	$\frac{5.7 \pm 0.3}{6.6}$	$\frac{10.5 \pm 0.5}{23.9}$	$\frac{4.7 \pm 0.2}{10.2}$	12.3 ± 0.6
<i>P. tremula</i> L.	59	$\frac{61.7 \pm 3.1}{3.3}$	$\frac{4.2 \pm 0.2}{4.5}$	$\frac{0.51 \pm 0.03}{4.5}$	$\frac{1.9 \pm 0.1}{4.4}$	10.8 ± 0.5
<i>Quercus iberica</i>	21	$\frac{66.7 \pm 3.3}{-}$	$\frac{3.1 \pm 0.2}{-}$	$\frac{0.49 \pm 0.02}{-}$	$\frac{1.1 \pm 0.1}{-}$	10.4 ± 0.5
<i>P. alba</i> L.	34	$\frac{89.6 \pm 4.5}{3.8}$	$\frac{6.4 \pm 0.3}{3.7}$	$\frac{0.88 \pm 0.04}{3.0}$	$\frac{4.6 \pm 0.2}{7.0}$	9.7 ± 0.5
<i>M. sylvestris</i> Mill.	45	$\frac{25.3 \pm 1.3}{3.2}$	$\frac{3.9 \pm 0.2}{5.6}$	$\frac{0.12 \pm 0.01}{3.6}$	$\frac{0.65 \pm 0.05}{7.1}$	10.4 ± 0.5
<i>A. negundo</i> L.	80	$\frac{50.5 \pm 2.5}{4.0}$	$\frac{8.5 \pm 0.4}{7.2}$	$\frac{0.38 \pm 0.02}{7.0}$	$\frac{4.7 \pm 0.2}{10.9}$	12.2 ± 0.6
<i>E. argentea</i> Pursch.	38	$\frac{37.2 \pm 1.6}{3.8}$	$\frac{9.5 \pm 0.4}{5.8}$	$\frac{0.33 \pm 0.02}{7.4}$	$\frac{5.5 \pm 0.3}{25.5}$	7.5 ± 0.4
<i>B. pendula</i> Roth.	77	$\frac{135.1 \pm 6.8}{5.6}$	$\frac{5.9 \pm 0.3}{4.7}$	$\frac{0.60 \pm 0.03}{4.0}$	$\frac{5.7 \pm 0.3}{12.1}$	6.5 ± 0.3
<i>S. alba</i> L.	40	$\frac{79.5 \pm 4.1}{3.6}$	$\frac{3.9 \pm 0.3}{4.8}$	$\frac{0.19 \pm 0.01}{6.0}$	$\frac{3.9 \pm 0.2}{8.1}$	9.0 ± 0.5
<i>U. minor</i> L.	76	$\frac{32.4 \pm 1.6}{3.7}$	$\frac{4.3 \pm 0.2}{5.4}$	$\frac{0.19 \pm 0.01}{6.0}$	$\frac{3.9 \pm 0.2}{8.1}$	11.5 ± 0.6
<i>U. laevis</i> L.	55	$\frac{7.3 \pm 1.4}{3.6}$	$\frac{3.1 \pm 0.2}{10.6}$	$\frac{0.13 \pm 0.01}{6.3}$	$\frac{1.0 \pm 0.1}{7.6}$	11.2 ± 0.6
<i>U. glabra</i> L.	25	$\frac{24.8 \pm 1.2}{-}$	$\frac{2.7 \pm 0.1}{-}$	$\frac{0.16 \pm 0.01}{-}$	$\frac{2.0 \pm 0.1}{-}$	10.5 ± 0.5
<i>F. excelsior</i> L.	26	$\frac{35.1 \pm 1.8}{-}$	$\frac{7.6 \pm 0.4}{-}$	$\frac{0.44 \pm 0.02}{-}$	$\frac{4.9 \pm 0.2}{-}$	9.0 ± 0.5
<i>S. vulgaris</i> L.	67	$\frac{41.7 \pm 2.1}{4.1}$	$\frac{6.5 \pm 0.3}{5.1}$	$\frac{0.38 \pm 0.02}{7.0}$	$\frac{5.8 \pm 0.3}{14.8}$	8.2 ± 0.4
<i>S. aucuparia</i> L.	22	$\frac{25.4 \pm 1.3}{2.4}$	$\frac{3.4 \pm 0.2}{4.3}$	$\frac{0.32 \pm 0.02}{9.0}$	$\frac{4.6 \pm 0.2}{11.1}$	9.6 ± 0.5
<i>R. canina</i> L.	56	$\frac{15.1 \pm 0.8}{2.7}$	$\frac{1.9 \pm 0.1}{4.2}$	$\frac{0.07 \pm 0.005}{4.0}$	$\frac{0.57 \pm 0.03}{4.8}$	7.5 ± 0.4
<i>C. oxyacantha</i> L.	29	$\frac{72.3 \pm 3.6}{-}$	$\frac{6.9 \pm 0.3}{-}$	$\frac{6.9 \pm 0.3}{-}$	$\frac{0.47 \pm 0.02}{-}$	8.7 ± 0.4

(c) Recommended plant species for bioindication heavy metals

Species	Zn	Cu	Cd	Pb
<i>Acer negundo</i> L.	+	+	–	+
<i>Betula pendula</i> Roth.	+	–	+	+
<i>Populus nigra</i> L.	+	+	+	+
<i>Syringa vulgaris</i> L.	–	+	–	+
<i>Salicaceae</i>	–	–	+	–
<i>Ulmaceae</i>	+	+	+	–

from studied cities compared to background values was several times higher [11]. For elements such as Zn and Cd, the difference in concentration between species at background sites were 5- and 12-fold, respectively, whereas under urban conditions these differences reached 20- and 190-fold (Table 1a). The indicative and accumulative abilities of the studied species for these elements increase significantly. Leaves collected in industrial and transport zones accumulate more heavy metals than those collected in residential and recreational zones. The greatest difference in the content of the studied elements in plant leaves between the zones were noted for Sumgayit, the smallest – for Barda region. On average, there is a threefold range of concentration variation depending on the functional zone of the city for metals such as Zn and Cu, and a fourfold range for Pb and Cd. In particular, for Sumgayit, the contrast between the metal content in the leaves of different zones of the city reaches 6 times for zinc and copper and 10 times for Cd and Pb. The presence of metals in the leaves of plants growing in Sumgayit, compared to other regions, is primarily associated with the level of pollution in the regions, which is one of the highest in Azerbaijan Republic (Fig. 1).

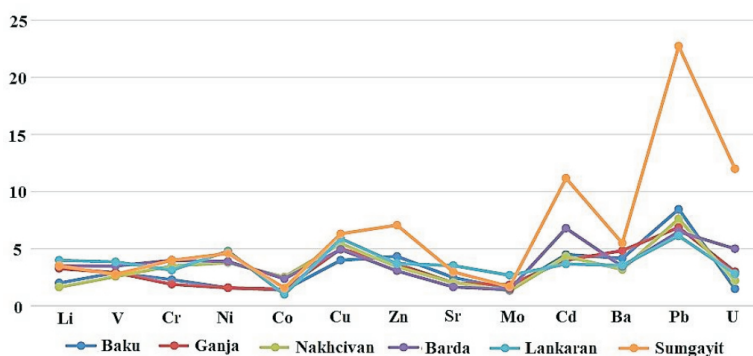
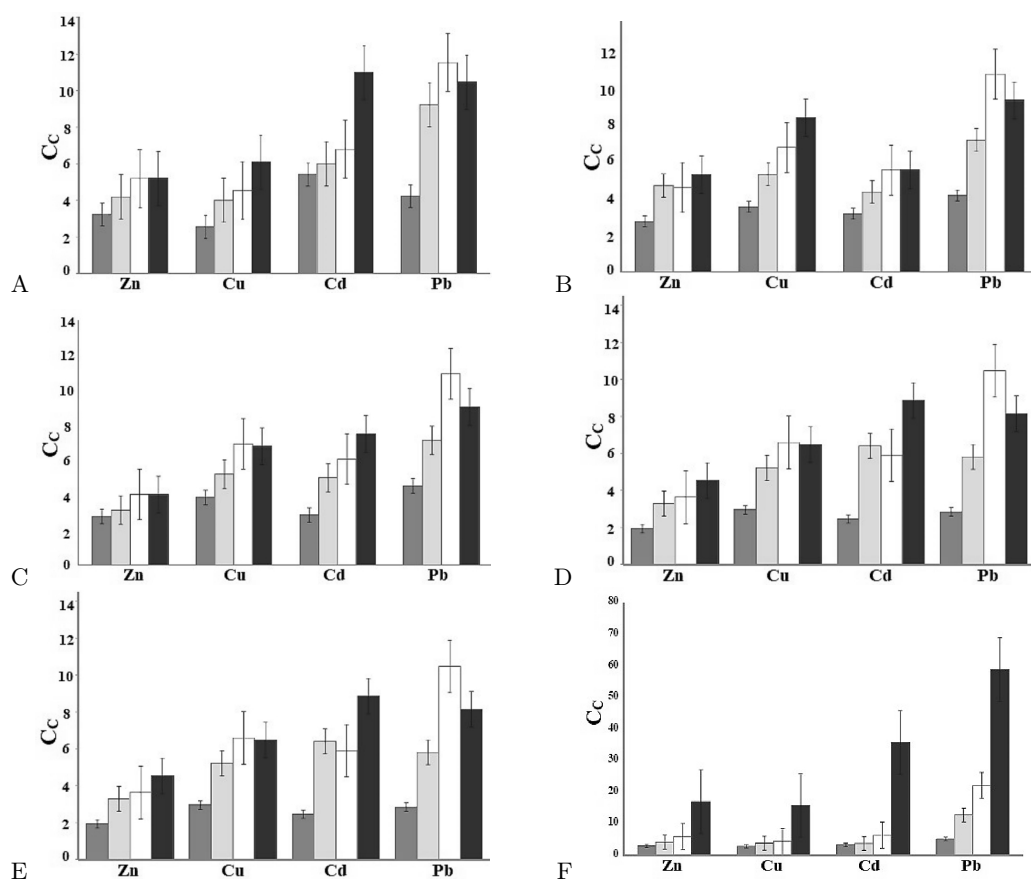


Fig. 1. C_c of chemical elements in leaves of trees and shrubs of the studied cities of Azerbaijan

According to Fig. 1, the average content of elements in the leaves of trees and shrubs in the studied Azerbaijan cities exceeds background values. All studied cities are characterized by the accumulation of Cd and Pb by plant leaves, as

well as Li, Ni and U for Sumgayit, Cr and Cu for Nakhchivan and Cu and Ni for Lankaran. The established dependencies can be explained by the fact that the industrial zone is a centre of concentration of enterprises with different specializations, where the sources of environmental pollution with heavy metals are the raw materials and the production process itself. In this work, the bioge indication capacity of leaves of dominant trees and shrubs growing in the zone of action of large industrial enterprises was studied in more detail. The elemental composition of leaves of trees and shrubs growing in the zone of influence of the complex of enterprises was analyzed (Ganja Machine-building Factory, Lankaran Instrument-making, Baku Shipyard, Sumgayit Glass Factory, Barda Brick Factory, etc.). Due to long-term industrial activity, artificial geochemical anomalies with elevated levels of environmental pollutants have formed around the sites. The residential zone has the lowest environmental pollution, since residential buildings represent a barrier to the spread of pollution from highways, and the density of vegetation is higher than in other areas. For the recreational zone, the established elevated concentrations of metals are associated with the proximity of major highways. The study revealed species of trees and shrubs whose leaves have a high accumulation capacity for heavy metals. As regards Zn, the maximum concentration capacity was observed by *Betula pendula* Roth., *Acer negundo* L. and leaves of trees of the genus *Populus*; for Cu – by *Acer negundo* L., *Elaeagnus argentea* Pursch., *Syringa vulgaris* L., *Ulmus minor* L. and *Populus nigra* L.; for Cd – by leaves of trees of the *Salicaceae* family; and for Pb – in *Betula pendula* Roth., *Syringa vulgaris* L., *Acer negundo* L., *Elaeagnus argentea* Pursch (Fig. 2a–f). These plants also show significant variability in the accumulation of the studied elements, a high maximum to minimum content ratio excess over background levels, and high accumulation coefficients.

Ash content is an important biogeochemical indicator characterizing the ratio of mineral and organic substances in a plant. The higher the ash content, the better the plant is adapted to the growing conditions and it can be considered an indicator of the adaptability of plant communities to environmental conditions [13]. Significant interspecific differences have been identified for content in leaves of different plant species. Ash content provides insight into the degree of air pollution, reflecting the gas absorption capacity of plants (Table 1a, b). According to the average ash content of leaves of tree and shrub species of plants, significant interspecific differences are observed. The highest ash content was recorded in the leaves of *Populus nigra* L., *Acer negundo* L., *Ulmus major* L. – approximately 12% on average cities, indicating a high gas absorption capacity consistent with findings from other authors. The lowest ash content was recorded in *Betula pendula* Roth., *Quercus iberica* and *Elaeagnus argentea* Pursch. averaging around 6% in regional samples. The obtained results are in agreement with numerous literary data from other authors, which show that these plant species have the greatest accumulating capacity for heavy metals and are applicable to biogeochemical indication [1–3,10].



Note: a) Baku; b) Ganja; c) Barda; d) Lankaran; e) Nakhcivan; f) Sumgayit

Fig. 2. C_c of heavy metals in the plants leaves depending on functional zones of regions

It is recommended to use these plant species in urban landscaping as natural filters for purifying atmospheric air (Table 1c). Table 1b presents average data on the accumulation of heavy metals and ash content of leaves in all studied regions. The average concentration of heavy metals in terrestrial plants is as follows: Zn – 30.0; Cu – 8.0; Cd – 0.035; Pb – 1.25 [11]. The problem of plant organisms' resistance to adverse factors of the urban environment has remained relevant for many years. Plants adapt to extreme conditions at different levels of biological organization in different ways. Concentrations of toxicants in plants of the studied regions allow us to identify in more detail the environmental factors that affect the condition and vital activity of plants [12,13].

Conclusion. The analysis of tree and shrub leaves in major cities of northern, eastern, and central Azerbaijan revealed notable accumulation of Ba, Cu, Cd, Pb, Zn, Cr, and U. Concentrations in urban areas exceeded background levels up

to 23-fold, with the highest values recorded for Pb. Metal accumulation varied by functional zone, being greatest in industrial and transport areas, and showed clear species-specific dependencies. Certain plant species can thus serve as reliable biogeochemical indicators and be used in urban greening. Among the studied cities, Sumgayit exhibited the highest accumulation of Cd, Pb, and U, reflecting the impact of nearby industrial facilities.

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¹*Department of Molecular Biology and Biotechnologies, Faculty of Biology, Baku State University, 23 Acad. Z. Khalilov St, AZ 1148*
 e-mail: roza.mammadova.nazim@bsu.edu.az,
<https://orcid.org/0009-0002-9934-0875>

²*Laboratory of Microelements and Microfertilizers, Institute of Soil Science and Agrochemistry, Ministry of Science and Education of the Republic of Azerbaijan, Baku, 5 M. Rahim St*
 e-mail: s.salimova@rambler.ru, <https://orcid.org/0009-0002-9934-0875>

³*Department of Soil Genesis, Geography and Cartography, Institute of Soil Science and Agrochemistry, Ministry of Science and Education of the Republic of Azerbaijan, Baku, 5 M. Rahim St*
 e-mails: sultanhuseynova@rambler.ru, <https://orcid.org/0000-0002-7991-3616>
gunay.mammadova@tai.science.az, <https://orcid.org/0000-0001-5196-4684>
cafarova@gmail.com, <https://orcid.org/0009-0001-7844-7756>

⁴*Department of Biology, Faculty of Natural Sciences, Sumgayit State University, Sumgayit, Azerbaijan, 1 Baku St, AZ5008*

⁵*Department of Soil Science and Real Estate Cadastre, Faculty of Ecology and Soil Science, Baku State University, Baku, Azerbaijan, 33 Acad. Z. Khalilov St, AZ1148*
 e-mail: turkanhesenova@mail.ru, <https://orcid.org/0000-0002-5040-2599>

⁶*Department of Ecological Chemistry, Faculty of Ecology and Soil Science, Baku State University, Baku, Azerbaijan, 33 Acad. Z. Khalilov St, AZ1148*
 e-mail: hicranrafiyeva@bsu.edu.az, <https://orcid.org/0000-0003-0782-4072>