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ELEMENTAL COMPOSITION OF THE ASH OF POPLAR LEAVES AS AN INDICATOR OF TECHNOGENESIS ON THE EXAMPLE OF THE TERRITORY OF SOUTH KAZAKHSTAN

One of the most important problems facing the community is the progressive pollution of the environment by technogenic factors. To obtain a general picture of pollution and the degree of impact on the environment, an integrated approach is required when studying the ecological state of the territory of Southern Kazakhstan. The article presents original data on the ecological and geochemical characteristics of the distribution of chemical elements in the ash of leaves of pyramidal poplar (*Populus nigra f. pyramidalis*), since this substrate accumulates pollutants from the environment. Analytical studies were carried out in the laboratory of Tomsk Polytechnic University using the INAA method (instrumental neutron activation analysis). Statistical parameters showed that Ca, Rb, Sr have a normal distribution, uneven distribution is typical for: As, Ag, Nd, Tb, Yb, Cr, Br, Sb, Cs, Ba, Sm, Eu, Lu, Ta, Au. The conducted cluster analysis showed 7 significant associations of chemical elements. In order to identify regional specifics, geochemical series were built relative to the clark of the noosphere, the relative average composition of living matter and literature data. The results of the analysis showed that the specific elements in the ashes of the pyramidal poplar leaves collected in the territory of South Kazakhstan are Na, Ca, As, Sr, Ag, Sb, Ba, Ta, U.

Key words: elemental composition, South Kazakhstan, bioindicator, pyramidal poplar leaf ash (*Populus nigra f. pyramidalis*), instrumental neutron activation analysis.

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Оңтүстік Қазақстан территориясының мысалында техногенездің көрсеткіші ретіндегі терек жапырақтар күлінің элементті құрамы

Қоғам алдында тұрған маңызды мәселелердің бірі – қоршаған ортаның техногендік факторлармен үдемелі ластануы. Ластанудың жалпы көрінісін және қоршаған ортаға әсер ету дәрежесін алу үшін Оңтүстік Қазақстан аумағының экологиялық жағдайын зерттеу кезінде кешенді тәсіл қажет. Мақалада пирамидалық терек (*Populus nigra f. pyramidalis*) жапырақтарының күліндегі химиялық элементтердің таралуының экологиялық және геохимиялық сипаттамалары туралы түпнұсқа деректер келтірілген, өйткені бұл субстрат қоршаған ортадан ластаушы заттарды жинайды. Аналитикалық зерттеулер Томск политехникалық университетінің зертханасында INAA әдісімен (нейтронды активтендірудің аспаптық талдауы) қолданылды.

Статистикалық параметрлер Ca, Rb, Sr қалыпты таралуын көрсетті, біркелкі емес таралу: As, Ag, Nd, Tb, Yb, Cr, Br, Sb, Cs, Ba, Sm, Eu, Lu, Ta, Au элементтеріне тән. Жүргізілген кластерлік талдау химиялық элементтердің 7 маңызды ассоциациясын көрсетті. Аймақтық ерекшеліктерді анықтау үшін кларк ноосферасына, тірі заттың салыстырмалы орташа құрамы мен әдебиет деректеріне қатысты геохимиялық қатарлар салынды. Талдау нәтижесі Оңтүстік Қазақстан аумағында жиналған пирамидалық терек жапырақтарының күліндегі ерекше элементтер Na, Ca, As, Sr, Ag, Sb, Ba, Ta, U екенін көрсетті.

Түйін сөздер: элементтік құрамы, Оңтүстік Қазақстан, биоиндикатор, пирамидалық терек жапырақ күлі (*Populus nigra f. pyramidalis*), нейтронды активтендірудің аспаптық талдауы.

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Элементный состав золы листьев тополя как индикатора техногенеза на примере территории Южного Казахстана

Одной из важнейших проблем, стоящих перед сообществом, является прогрессирующее загрязнение окружающей среды техногенными факторами. Для получения, общей картины загрязнения и степени воздействия на окружающую среду, необходим комплексный подход при изучении экологического состояния территории Южного Казахстана. В статье приведены оригинальные данные об эколого-геохимической характеристике распределения химических элементов в золе листьев тополя пирамидального (*Populus nigra f. pyramidalis*), так как данный субстрат аккумулирует в себе загрязнения из окружающей среды. Аналитические исследования проведены в лаборатории Томского политехнического университета методом ИНАА (инструментальный нейтронно-активационный анализ). Статистические параметры показали, что Ca, Rb, Sr имеют нормальное распределение, неравномерное распределение характерно для: As, Ag, Nd, Tb, Yb, Cr, Br, Sb, Cs, Ba, Sm, Eu, Lu, Ta, Au. Проведенный кластерный анализ показал 7 значимых ассоциаций химических элементов. С целью выявления региональной специфики были построены геохимические ряды относительно кларка ноосферы, относительного среднего состава живого вещества и литературных данных. Результаты анализа показали, что специфичными элементами в золе листьев тополя пирамидального собранного на территории Южного Казахстана являются Na, Ca, As, Sr, Ag, Sb, Ba, Ta, U.

Ключевые слова: элементный состав, Южный Казахстан, биоиндикатор, зола листьев тополя пирамидального (*Populus nigra f. pyramidalis*), инструментальный нейтронно-активационный анализ.

Introduction

Environmental pollution is a major problem of the modern world. Natural and anthropogenic factors negatively affect the state of ecosystem components, causing an urgent need to monitor and assess the quality of the natural environment. A special role is played by contamination of atmospheric air and changes in its chemical composition in connection with developed processes of technogenesis, which is the most important risk factor for human health. For example, trace elements coming from industrial enterprises are persistent and widely dispersed in the environment. They interact with various natural components and have a toxic effect on the biosphere. They are emitted into the urban atmosphere as airborne particles of different sizes in the form of solid or liquid particles [1, 2].

Higher plants are used as bioindicator as organisms that contain information about the qualitative assessment of the environment. With the help of indicator plants, it is possible to distinguish the degree of pollution, distinguish pollution sources and their impact zones, identify polluting chemical components and map metallic air pollution in urban areas [3, 4].

Many researchers have proved that poplar is one of such plants [5-9]. Poplar leaves accumulate

heavy metals and are mainly used in biomonitoring studies [10-12].

The elemental composition of plants depends on environmental factors, climatic and landscape-geochemical growing conditions [13,14]. Chemical elements (CE) play a significant role in the growth and development of a plant organism at all stages of the plant life cycle. Many domestic and foreign scientists have studied the elemental composition of plants [15-20].

The purpose of the work was to conduct an environmental assessment of the content and characteristics of the accumulation of chemical elements in the leaves of pyramidal poplar (*Populus nigra f. pyramidalis*) using the example of Southern Kazakhstan.

Materials and methods

As an object of study, we took the leaves of the plant *Populus nigra f. pyramidalis*, which we selected in Southern Kazakhstan. The reason for choosing poplar is its frequent use for landscaping purposes. Also the peculiarity of the leaf plate structure allows them to accumulate chemical elements.

Poplar leaves were sampled in dry weather at a height of 1.5-2 m according to the recommendations [21]. Poplar is widespread in green plantations

in South Kazakhstan. Trees from which leaf samples were taken were selected on the basis of approximately the same age and height. All the trees studied are about 50 years old. Poplar trees are commonly planted along streets and in park plantings. A total of 37 samples were collected. Sample preparation (sampling, packing, drying to constant weight, averaging samples before further studies) allowed representative samples to be obtained. Poplar leaves were sampled using the mean sampling method, at each location leaves were collected from 3 rows of growing trees of approximately the same age and height. The leaves were packaged in paper bags. They were dried at room temperature to a constant sample weight. Next, they were pulverized and weighed. Then they were ashed at 450 °C by dry mineralization method for 5 hours to constant weight. This procedure allowed us to calculate the ashing ratio. Then further calculations were carried out on dry mass according to the requirements of State Standard 26929-94 [22].

The amount of dust settled on the plant under study can be directly related to the level of air pollution with heavy metals such as lead, mercury, cadmium, etc. However, the presence of rain or changing seasons significantly affects the amount of dust settled. Therefore, according to the methodology, in order to determine the pollutants trapped on the surface of leaves, samples are not

washed but dried immediately at room temperature in a ventilated room.

Results and Discussion

During the study, 28 chemical elements were studied and analyzed in the ash of poplar leaves (*Populus nigra f. pyramidalis*). Most elements had an uneven distribution, which is confirmed by statistical data (Table 1).

According to the data obtained, the elements calcium, rubidium and strontium have a normal distribution, which is noticeable by the slight variation in the maximum and minimum values, as well as the correspondence of the average and median values. The elements sodium, scandium, iron, cobalt, zinc, lanthanum, cerium, hafnium, thorium, uranium can also be classified as elements with a distribution close to normal.

So on insignificant scatter and correspondence of average to median value we can judge about normal distribution of elements Ca, Rb, Sr, and also close to normal for elements Na, Sc, Fe, Co, Zn, La, Se, Hf, Th, U. Uneven distribution with coefficient of variation more than 70% can be observed for elements As, Ag, Nd, Tb, Yb and elements with coefficient of variation more than 100% – Cr, Br, Sb, Cs, Ba, Sm, Eu, Lu, Ta, Au. Uneven distribution of chemical elements most likely indicates the presence of an anthropogenic factor.

Table 1 – Statistical parameters of distribution of chemical elements in ash of leaves of poplar pyramidal (*Populus nigra f. pyramidalis*) on the territory of South Kazakhstan.

Elements	Mean	Standard error	Geometric mean	Median	Moda	min	max	V, %
Na	20924	1898	18822	21010	38940	7700	40000	48
Ca	115079	6958	109726	110000	106400	46800	181900	29
Sc	0,58	0,06	0,51	0,5	0,3	0,17	1,3	52
Cr	11	3,541	4,88	4,7	Multiple	0,07	92	213
Fe	2141	221	1922	2010	Multiple	760	5550	51
Co	16	1,7	15	14	22,8	3,3	36	50
Zn	956	131	786	922	1210	138	3261	68
As	5,7	0,87	4,5	4,5	7,52	1,1	19	73
Br	3,3	0,85	1,53	2,0	2	0,05	18	138
Rb	30	2,7	27	25	25	10	59	46
Sr	3480	249	3243	3473	2515	1494	6566	35
Ag	1,2	0,21	0,81	0,95	0,15	0,15	3,5	89
Sb	0,31	0,08	0,23	0,22	0,12	0,08	2,3	138
Cs	0,54	0,33	0,19	0,22	0,05	0,04	6,4	244

Elements	Mean	Standard error	Geometric mean	Median	Moda	min	max	V, %
Ba	130	44	82	64	Multiple	24	1051	150
La	1,7	0,19	1,5	1,5	1,53	0,55	4,7	56
Ce	3,9	0,50	3,2	3,5	3,43	1,0	9,7	66
Nd	1,8	0,30	0,96	1,2	0,45	0,11	5,6	97
Sm	0,22	0,05	0,1	0,16	0,02	0,01	1,05	107
Eu	0,03	0,008	0,01	0,02	0,003	0,001	0,12	101
Tb	0,02	0,005	0,02	0,01	0,01	0,002	0,10	84
Yb	0,13	0,02	0,1	0,12	Multiple	0,004	0,47	72
Lu	0,02	0,004	0,01	0,007	0,003	0,002	0,08	102
Hf	0,19	0,03	0,15	0,14	0,09	0,04	0,43	63
Ta	0,04	0,009	0,02	0,02	0,005	0,005	0,18	126
Au	0,02	0,007	0,007	0,006	0,002	0,0002	0,16	162
Th	0,53	0,065	0,5	0,5	Multiple	0,11	1,4	58
U	1,08	0,11	0,8	0,96	0,41	0,23	2,8	61

To characterize the intensity of biological accumulation of chemical elements by leaves of pyramidal poplar (*Populus nigra f. pyramidalis*) from underlying surfaces, we calculated the coefficient of biological absorption (BAC), which was calculated relative to A.N. Grigoriev [23]. According to the results of the calculation, a series of biological accumulation of chemical elements by poplar leaves was constructed:

BAC = Sr₁₃ – Zn₁₃ – Ag₁₁ – Au₅ – Ca₃ – Na₁ – As₁.

According to the series of biological uptake of elements according to A.I. Perelman, strontium, zinc, calcium, and sodium are included in the group of strong biological accumulation, its CBA value varies from n to 10n. Vital elements are calcium, sodium, zinc; arsenic is conditionally essential element; strontium, gold and silver are toxic elements or abiogenic with strontium can substitute calcium in living matter [24].

To understand the nature of accumulation of chemical elements and the associations they form, we conducted a cluster analysis (Figure 1), which allowed us to identify several significant associations of chemical elements: 1 – Ta, Ce; 2 – Lu, Sm, Hf, Th, Yb, Fe, La, Sc; 3 – Ba, Sb, As; 4 – Tb, Ca; 5 – Ag, Rb, Br; 6 – Nd, Cr; 7 – U, Na.

Several groups of associations are clearly identified, among which we can single out elements related to dust-aerosol industrial emissions, for example,

emissions from thermal power plants (Lu, Sm, Hf, Th, Yb, Fe, La, Sc), to petrochemical production (Ag, Rb, Br). The association of barium, antimony, arsenic may indicate barite deposits in the study area, the presence of these elements on the surface of the leaf lamina most likely indicates their ingress from atmospheric air. For example, the maximum values of barium – 1051 mg/kg were recorded near the city of Shymkent in the village of Arys, which is located near the Badam barite-fluorite deposit.

When normalizing the content of chemical elements in ash of poplar pyramidal to the noosphere clark [25] and to the average composition of living matter [26], the biogeochemical series of accumulation looks as follows:

Kc relative to the noosphere clark – Sr₈₇ > Au₂₉ > Ag₂₄ > Zn₂₁ > Ca_{7,2} > Ba_{3,6} > As_{1,9} > Sb_{1,2} > Na_{1,1}.

Kc relative to the average composition of living matter – Zn₁₉₁ > Sr₁₇₄ > Na₁₀₅ > Co₈₀ > Ca₂₃ > Fe₂₁ > As₁₉ > Rb₆ > Cs_{5,4} > Ba_{4,3} > Br_{2,2}.

As can be seen from both biogeochemical series, the common chemical elements are sodium, calcium, zinc, arsenic, strontium, barium, which accumulate in fairly high concentrations in the ash of the leaves of *Populus nigra f. pyramidalis*.

High concentrations of zinc, sodium and calcium can be explained by the fact that they are essential elements involved in the regulation of metabolic processes and the maintenance of general homeostasis in the plant.

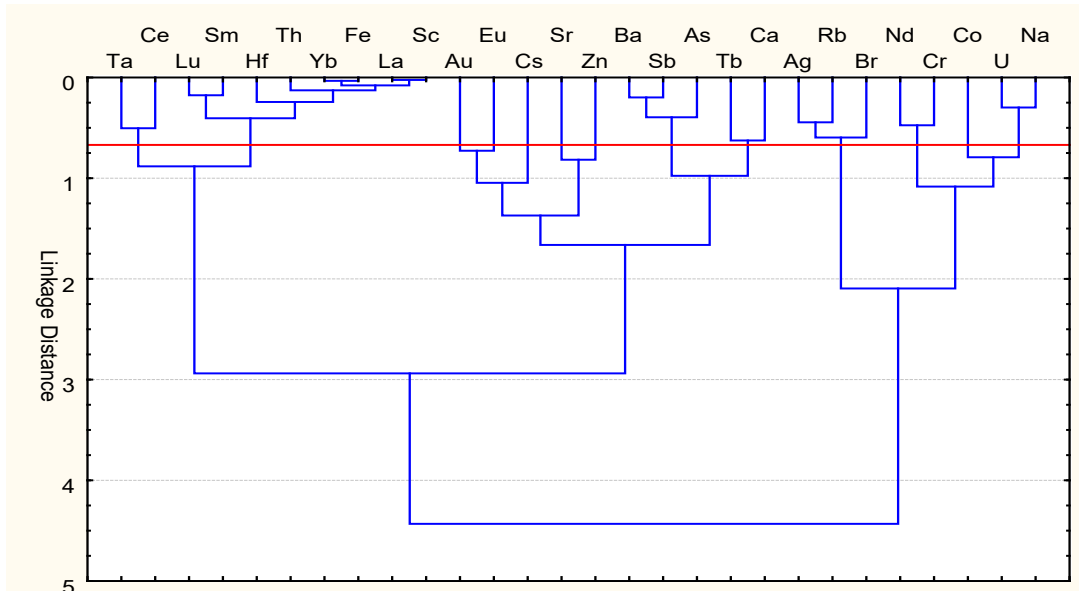
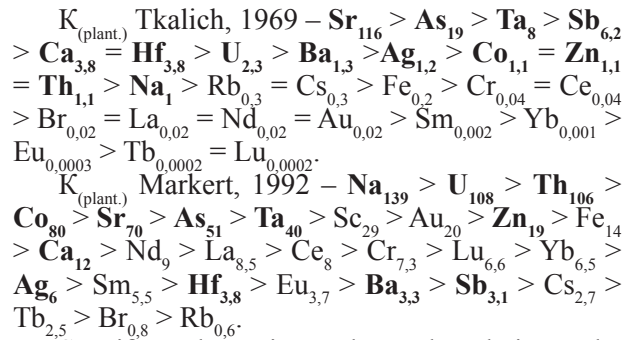
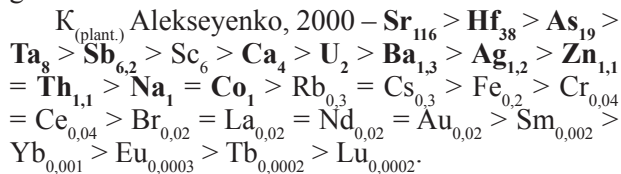


Figure 1 – Dendrogram of correlation matrix of geochemical spectrum of chemical elements in ash of leaves of poplar pyramidal (*Populus nigra f. pyramidalis*) growing on the territory of South Kazakhstan

Strontium, barium and arsenic can be classified as toxic elements. High concentrations of these CEs in a plant may indicate the influence of a technogenic factor. Sources of pollution can be industrial enterprises, vehicles, waste burning, etc. Also, these elements can be actively absorbed from water, for example, strontium is a specific element for salt formations in drinking water in the study area [27]. The presence of high concentrations of barium can be explained by the fact that this element is concentrated by plants, and also under conditions of environmental pollution with sulfur compounds, many elements form poorly soluble sulfides, as a result of which strontium and barium remain in soil solutions [25]. In general, the reasons for the high concentrations of barium, arsenic and strontium in the leaf ash of *Populus nigra f. pyramidalis* can be complex and influenced by many factors, including geological, anthropogenic and biological.

To identify regional geochemical features, the results obtained were compared with literature data [28-30]. According to the results of comparison with the average content in plant ash the following biogeochemical series was constructed:



Specific to the region under study, relative to the literature data are the following elements sodium, uranium, thorium, cobalt, strontium, arsenic, tantalum, zinc, calcium, silver, hafnium, barium, antimony.

We also carried out a comparative analysis of the data with the results obtained for some regions of Kazakhstan and Russia (Figure 2).

Figure 2 shows the results of comparison of elemental composition of poplar leaves growing on the territory of South Kazakhstan, Pavlodar region, Tomsk region (Russia). Relative to other regions, the ash of poplar leaves sampled on the territory of South Kazakhstan is characterized by an increased level of Na, Co, As, Sr, Ag, Cs, Ce, Nd, and U ($p < 0.001$). The presence of the above elements in poplar leaves possibly indicates polymetallic, iron and uranium deposits.

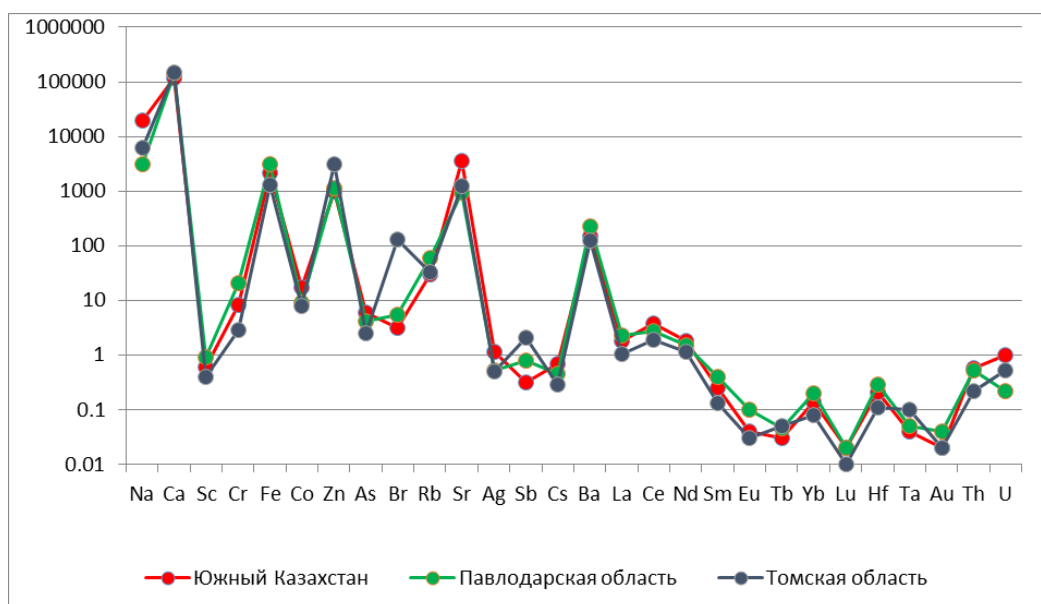


Figure 2 – Elemental composition of poplar leaf ash in some territories of Kazakhstan and Russia.

The results of the biogeochemical indicators of the study are summarized in Table 2. Chemical elements that are more often repeated in the biogeochemical indicators are highlighted in bold. Ca-As-

Sr – repeated four times, Na-Ag-Sb-Ba-Ta-U – three times, which indicates a specific accumulation of CE data in the studied substrate on the territory of Southern Kazakhstan

Table 2 – Complex of biogeochemical indicators

Biogeochemical indicators	Chemical elements
Coefficient of variation more than 100%	Cr, Br, Sb , Cs, Ba , Sm, Eu, Lu, Ta , Au
Biological absorption coefficient	Ca , Zn, Sr , Ag , Au,
Associations of significant correlations	Na , Ca , Sc, Cr, Fe, As , Br, Rb, Ag , Sb , Ba , La, Ce, Nd, Sm, Tb, Yb, Lu, Hf, Ta , Th, U.
Concentration coefficient relative to clarke according to M.A. Glazovskaya (2007) and A.P. Vinogradova (1932)	Na , Ca , Zn, As , Sr , Ba .
Concentration coefficient relative to literature data	Ca , As , Sr , Sb , Hf, Ta , U.
Concentration of chemical elements relative to data for Kazakhstan and Russia	Na , Co, As , Sr , Ag , Cs, Ce, Nd, U.

Conclusion

According to the complex of biogeochemical indicators and their comparison with the data on poplar leaf ash in Pavlodar region (Kazakhstan) and Tomsk region (Russia) geochemical specificity of the studied region was established. The concentration of the following chemical elements: sodium, calcium, arsenic, strontium, silver, antimony, barium, tantalum, uranium is significantly higher in the studied region. It is assumed that the spectrum of the above elements

is associated with the mining of polymetallic and iron ores, petrochemical production and uranium mining. However, the source of the studied elements in the ash of the plant under study has not been fully studied and requires additional extensive research.

Conflict of interest

All authors have read and familiarized themselves with the content of the article and have no conflict of interest.

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