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Assessment of environmental pollution with rare-earth metals through bioaccumulation studies using vegetal bioindicators

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Abstract. Environmental pollution by anthropogenic activities has become a global concern as the release of organic and inorganic pollutants into the atmosphere is responsible for important health problems among the population. The rare-earth metals processing sector has raised particular problems due to the bioaccumulation potential of these metals in the food chain. Urban trees are able to retain pollutants from the environment and can be used as bioindicators also for the rare-earth metal pollution. This paper aimed to assess the bioaccumulation of some rare-earth metals, besides other metals and non-metals, in the foliar part of six urban tree species (*Populus nigra* L., *Populus tremula* L., *Populus x canadensis* Moench, *Betula pendula* Roth, *Aesculus hippocastanum* L. *and Fraxinus excelsior* L.) sampled from different areas of the municipality of Bucharest. Laboratory experiments have shown that all tree species used in the study are able to retain rare-earth metals, but the bioaccumulation capacity is species-specific.

Keywords: rare-earth metals, environmental pollution, bioaccumulation, spectrometry

1. Introduction

The anthropogenic influence on the environment that occurred during the last few decades has led to a significant depreciation of the environment quality, which has been implicitly reflected on the health of the population and ecosystems [1].

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Metals are among the hazardous anthropogenic substances released to the environment. Once arrived to the environment, metals do not decrease their level over time but accumulate continuously and in increasing amount correlated with the global population growth, expansion of industrial activities, increased use of fossil fuels, etc. [2], [3].

Rare-earth metals (REMs), a total of seventeen chemical elements that include the lanthanides group of fifteen elements, plus scandium and yttrium, are considered indispensable in many economic fields, such as agriculture, renewable energy (solar panels, wind turbines, rechargeable batteries), in manufacture of medical devices, smart phones, permanent magnets, weapons systems in national defense, hybrid engines, etc. [4], [5]. REMs are widespread in the earth's crust but they do not exist as individual native metals because of their high reactivity. Instead, they occur together in over 250 minerals as either minor or major constituents [6]. Rocks, such as granite or pegmatite, contain rare-earth metals in the form of phosphates, silicates, fluorides or carbonates.

The increasing use of the rare earth elements has raised concern about environmental toxicity, which may further cause harmful effects on human health [7], [8]. The biggest problem of rare-earth minerals is that they are associated with radioactive elements (particularly thorium and uranium). During the production cycle there is a considerable release, into the environment and groundwater, of hazardous chemicals and radioactive elements [4].

The world leader in the production of rare metals is P. R. of China; in 2017, China produced 81% of the world's rare-earth supply [9]. Total global reserves of such minerals are estimated at about 99 million tonnes, of which about 36 million tonnes are in China, 19 million tonnes in Russia and neighbouring countries and 13 million tonnes in the USA [10].

The availability of rare-earth metals in the environment is dependent on some natural factors such as the Earth's surface activities and the surface movements of the Earth's crust, such as volcanic eruptions, groundwater flow and neomorphism. The active and abandoned mines are the most important anthropogenic factor in the release of rare-earth metals into the environment [11], [12]. Rare-earth minerals processing is a complex technology that often involves solvent extraction and flotation processes, coupled with some electrolytic processes, but minimal research has been done on the recovery of harmful residuals [7].

Agricultural practices in which rare-earth elements are used in mineral fertilizers become sources of contamination of soil, surface water, groundwater and biota. The presence of high concentrations of rare-earth metals in soil can have severe consequences for the environment, including effects on groundwater and agricultural products. Under these conditions, rare-earth metals present in soil and water can enter the human body, especially by ingesting food, so these chemicals can be considered a risk to human health [8].

There are few data on the presence of rare-earth metals in the food chain; the real concern is their accumulation in the brain from 0.1 to 19.4 µg/g [13] and in ribs from 0.4 to 22.0 µg/kg [14]. Marzec-Wroblewska et al. found La (19.5 µg/kg), Ce

(41.9 µg/kg), Eu (0.68 µg/kg) and Gd (3.19 µg/kg) in human sperm [15]. De-la-Iglesia-Iñigo et al. published that rare-earth metals can induce abnormalities in red blood cells. Therefore, the concentration of REMs in agricultural soils and urban areas is important due to their likely bioaccumulation in plants as a result of anthropogenic activities [16].

Vegetation plays an important role as a natural filter that helps to improve air quality by storing dust particles on the surface of the leaves. Because the leafy surface of plants is permanently exposed to atmospheric air, it acts as a receptor for air pollutants. Biomonitoring of air quality with the help of various organisms is a practice used for several decades.

Rare-earth metals are absorbed by plants to a greater extent compared to other non-essential elements. Due to their greater mobility in the soil, light rare-earth metals (LREMs), such as La, Ce, Pr, Nd, Pm, Sm, Eu, are more easily assimilated by plants, being in a higher concentration in their tissues, as compared to heavy rare-earth metals (HREMs), such as Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y [17].

Understanding the anthropogenic sources of rare-earth elements, transfer mechanisms, bioaccumulation issues and their environmental behaviour requires more-in-depth studies to accurately assess the impact of REMs on human health [18].

This research aims to evaluate the bioaccumulation of the rare-earth metals along with other metals (Al, Ti, Si, Se, At, Re, In, Ga) in the foliar plant material of some tree species used as bioindicators in our study: *Populus nigra* L., *Populus tremula* L., *Populus x canadensis* Moench, *Betula pendula* Roth, *Aesculus hippocastanum* L. and *Fraxinus excelsior* L. The samples under investigation were taken from different areas of Bucharest municipality in October 2019. The bioaccumulation capacity of the rare-earth metals was assessed using the accumulation index (REMs-AI), and the results were compared with maximum allowable concentrations, as specified in the reglementations.

2. Materials and methods

The experiments were performed in the laboratories of the Institute of Biology Bucharest (IBB) of the Romanian Academy, and in the Laboratory of Applied Microbiology of the Faculty of Biotechnology within the University of Agronomic Sciences and Veterinary Medicine Bucharest, in compliance with specific norms and regulations.

For this study, samples of plant material were taken from the following 6 species of urban trees: *Aesculus hippocastanum* L., *Betula pendula* Roth, *Fraxinus excelsior* L., including 3 species of *Populus* (*Populus tremula* L., *Populus x canadensis* Moench and *Populus nigra* L.). The samples were collected from different areas of Bucharest, as follows: sample 1 from INCDIE ICPE-CA courtyard; sample 2 from the Botanical Garden "Dimitrie Brândză"; sample 3 from Panduri Street and samples 4, 5, 6 from USAMV Campus).

The samples were stored immediately after sampling, at a constant temperature of approximately -18 ° C, thus preventing their possible contamination.

Microbiological imprint of the vegetal samples on the nutrient medium was performed immediately after collecting the samples, using the method and the nutrient medium described by [19].

The nutrient medium was autoclaved at 121°C for 30 minutes, then distributed to the laminar flow hood in the 12 sterile Petri dishes, 3 for each species. The plates were incubated on a thermostat at 37°C for 48 h. The samples were stored in the refrigerator at a temperature between +0 - 5ºC.

Quantitative determination of the rare-earth elements and other metals from the vegetal samples was performed using the Rigaku Supermini X-ray fluorescence spectrometer owned by the X-ray Fluorescence Spectrometry Laboratory of the Institute of Biology Bucharest.

The stored vegetal samples were allowed to thaw, then dried at 80 ° C for 24 hours and ground into a fine powder. The powder was placed in Ø32 mm polyethylene containers, then the samples were placed in the special locations of the equipment, along with 2 other calibration samples, to be analyzed on the X-ray fluorescence spectrometer.

Bioaccumulation capacity of rare-earth metals was evaluated based on the REMs-AI index which represents the ratio between the total amount of accumulated rare-earth metals (mg / kg dry biomass) and the number of REMs accumulated by a perennial plant species.

3. Results and discussions

Samples of vegetal material that were subjected to X-ray fluorescence spectrometry analyzes came from species with the ability to accumulate metals, frequently spread especially in urban and industrial areas where air pollution is increased.

The period of sampling the vegetal material is particularly important for the relevance of the study. Therefore, the samples were collected in October 2019 so that the leaves of the trees are mature and have time to accumulate air pollutants.

Six samples of plant material were analyzed using X-ray fluorescence spectrometer, in helium and P10 gas flux, by irradiating them with an X-ray beam and recording the refraction intensity at a specific angle, in order to determine the amount of bioaccumulated rare-earth metals in the vegetal tissues (XRF method). Vegetal polymers degradation by various processes is a complex process involving tens to hundreds species and chemical reactions [20].

The measurement results highlighted the presence of 6 rare metals (Tb, Tm, Y, Dy, Eu, La) in the 6 tree species studied (Table 1). It was noted that the species *Betula pendula* Roth did not accumulate any rare-earth metals.

Table 1. The results of the XRF analysis revealing rare-earth metals

Plant species	**Sample code**	**Ash, (g)**	**Mineral type**	**Mineral conc. (%)**	**Mineral mass (g)**	**Metal weight, (mg)**
Populus nigra L.	1	0.0542	Tb_4O_7	1.7158	0.0930	79.1
Populus nigra L.	1	0.0542	Tm_2O_3	1.0495	0.0569	49.8
Aesculus hippocastanum L.	2	0.0512	Y_2O_3	0.1899	0.0097	7.7
Aesculus hippocastanum L.	2	0.0512	Dy_2O_3	1.0645	0.0545	47.5
Populus x *canadensis* M.	4	0.0552	Y_2O_3	0.8869	0.0490	38.6
Fraxinus excelsior L.	5	0.0507	Eu_2O_3	6.7175	0.3406	294.1
Fraxinus excelsior L.	5	0.0507	Tm_2O_3	1.9696	0.0999	87.4
Populus tremula L.	6	0.0288	La_2O_3	17.3406	0.4994	425.8
Populus tremula L.	6	0.0288	Eu_2O_3	1.3074	0.0377	32.5

Terbium (Tb) was accumulated only by *Populus nigra* L., lanthanum (La) by *Populus tremula* L., and dysprosium (Dy) by *Aesculus hippocastanum* L., while the other metals (Tm, Eu, Y) were accumulated by 2 species, ass seen in Figure 1. These results prove that the accumulation of rare metals varies from one species to another.

The study of Stan et al. (2001) on mosses samples harvested during the summer season in the northeastern part of Transylvania resulted in approximately 3.31 mg / kg La and 0.105 mg / kg Tb. These results indicated the highest amounts of bioaccumulated rare-earth metals compared to the results on samples in other areas, e.g Russia, Norway and Poland, the difference between the results being quite significant. Markert (1991) stated that under normal conditions, the reference values for lanthanides in plants are as follows: La - 0.15-0.25 mg / kg dry biomass; Y - 0.15-0.25 mg / kg dry biomass; Dy - 0.025-0.05 mg / kg dry biomass; Eu - 0.005-0.015 mg / kg dry biomass; Tb - 0.005-0.015 mg / kg dry biomass [21].

Our experiment indicated an excessive bioaccumulation of rare-earth metals in leaves, especially La (425.8 mg/kg dry biomass) and Eu (294.1 mg/kg dry biomass). The source of these metals could be precipitation, fertilizers, airborne particles, wastewaters etc. Lanthanum was bioaccumulated only by *Populus tremula* L., while Eu was accumulated both by *Populus tremula* L. (32.5 mg / kg dry biomass) but also by *Fraxinus excelsior* L. (294.1 mg / kg dry biomass).

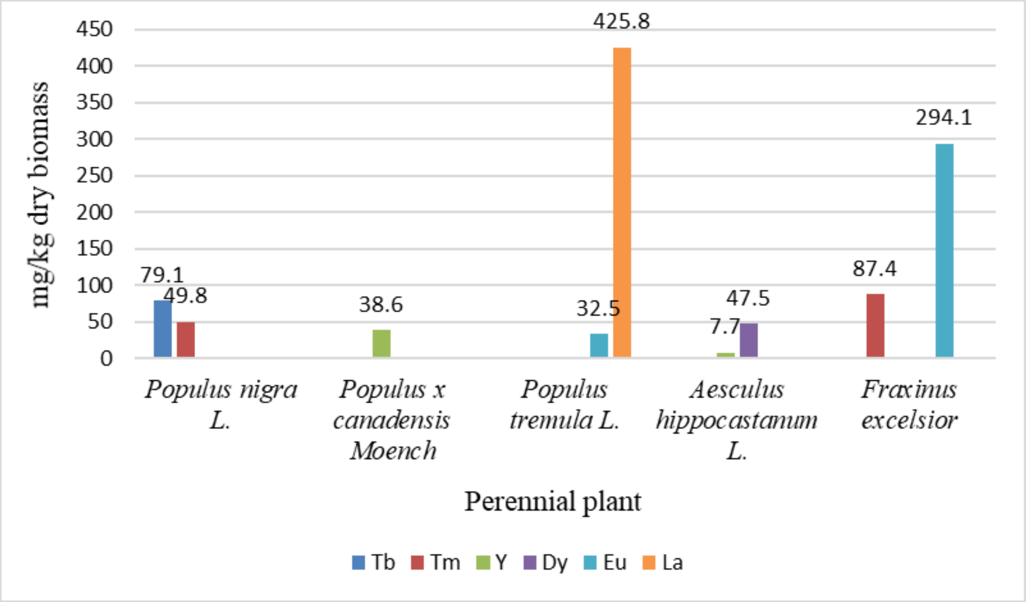

Fig. 1. Bioaccumulation of rare metals in tree species

Studies by Chunhong Zhang et al. prove that high concentrations of Eu can inhibit the development of callus or even lead to its death, and high concentrations of La may inhibit plant growth [22]. Research conducted by Brown et al. showed that La ions inhibited the opening of stomata on the plant surface, thus reducing the process of photosynthesis and transpiration of the plant [23].

Human exposure to La has been shown to induce pneumoconiosis [24], [25], a respiratory disease usually associated with miners. High amounts of La have also been found in brain tumor tissues in patients with astrocytoma compared to normal brain tissue [26].

Of the five species of trees that accumulated rare-earth metals, four accumulated two metals each, while *Populus x canadensis* Moench only one, namely yttrium (Y). This metal is very common in plants, the accumulation of yttrium being influenced by both biotic and abiotic factors. Hong et al. proved that yttrium is most accumulated in the root, then in the leaf and least in the stem [27]. However, this metal is not an essential element for the plant growth, but it can influence its life cycle, as data from the literature on yttrium are very few. Yttrium binds to biomolecules, forming complexes of compounds containing phosphorus, mucopolysaccharides and fluorine [28] but also binds to nucleic acids [29].

In the first paper published in 1913 by Evans on the influence of yttrium on a plant growth, it is mentioned that this metal produces a decrease in cell division [30].

The presence of yttrium in plants can be explained by the amount of yttrium in the soil due to lithogenesis and pedogenesis, the chemical composition of rocks and minerals, the physical and chemical properties of the soil, but also anthropogenic factors. Traces of plant yttrium (Y) in *Populus x canadensis* Moench and *Aesculus* *hippocastanum* L. could also have been caused by the 1986 Chernobyl nuclear accident.

Scientists showed that Tb in concentrations of 23-819 mg/kg dry biomass and Dy in concentrations of 1-78 mg / kg dry biomass can inhibit the growth of root and shoots in *Asclepias syriaca* [11].

In the experiments of this research, Tb was bioaccumulated in a concentration of 79.1 mg/ kg dry biomass in *Populus nigra* L., while Dy in concentration of 47.5 mg/kg dry biomass in *Aesculus hippocastanum* L.

Comparing the bioaccumulation of rare-earth metals in the three species of poplar sampled for this study *(Populus tremula* L., *Populus nigra* L. *and Populus x canadensis* Moench), it was shown that the plants accumulated different rare metals in different concentrations, as seen in Figure 2. *Populus tremula* L. accumulated very large amounts of lanthanum (425.8 mg/kg dry biomass).

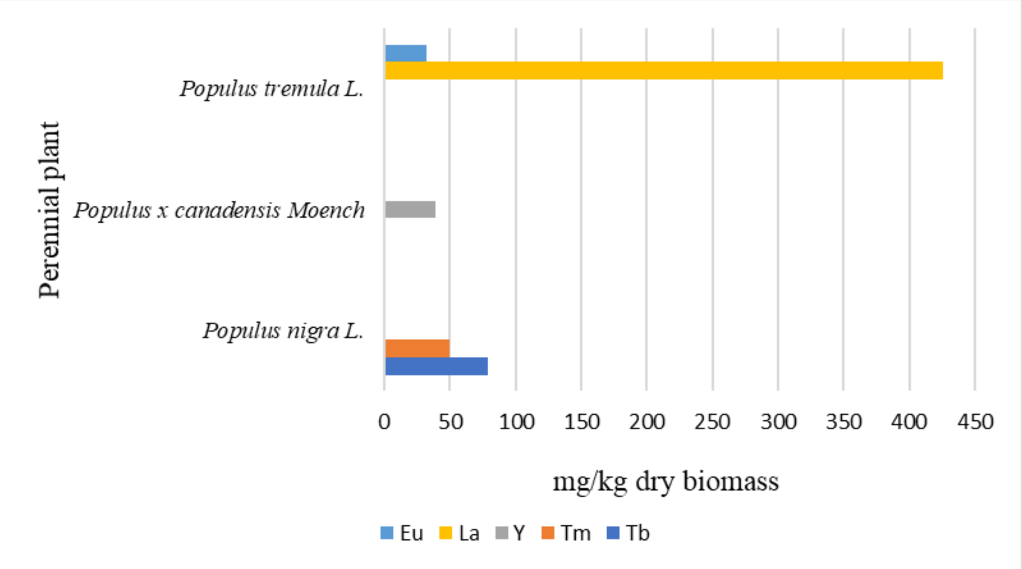

Fig. 2. Bioaccumulation of rare metals in poplar species

The bioaccumulation capacity of rare-earth metals of different species was assessed using the accumulation index (MR-AI); values are presented in Table 2.

Table 2. Accumulation index of the tree species used in this research

Plant species	**REMs-AI**
Populus nigra L.	64.45
Populus x *canadensis* Moench	38.6
Populus tremula L.	229.15
Fraxinus excelsior L.	190.75
Aesculus hippocastanum L	27.6

As seen in Table 2, the highest value of the accumulation index occurs in *Populus tremula* L., about 10 times higher than that of the species *Aesculus hippocastanum* L. *Fraxinus excelsior* L. and *Populus tremula* L. are the species that have accumulated the most rare-earth metals and could be used as bioindicator species to evaluate the REMs bioaccumulation. The image in Figure 3 shows that the light rare-earth metals (LREMs), namely Y, La, Eu, were accumulated in larger quantities in the investigated plants compared to heavy rare-earth metals (HREMs), the difference in bioaccumulation being just significant. One explanation for this could be that LREMs are much more common, easily extractable, and are found in a higher concentration in the continental crust than HREMs [31].

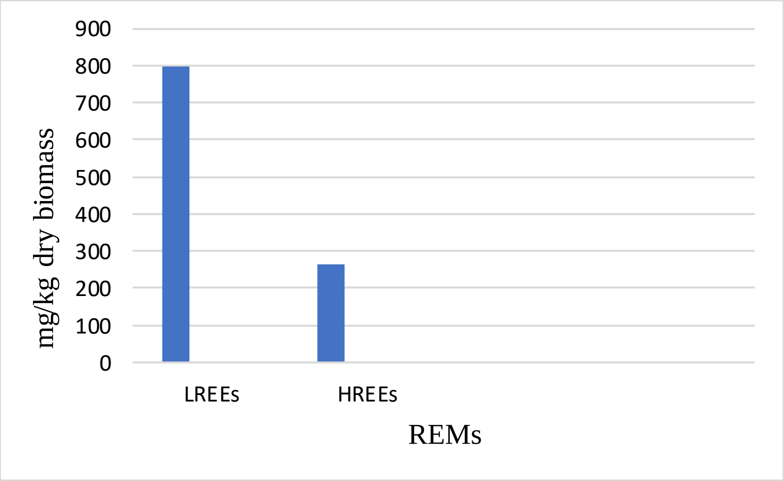

Fig. 3. Accumulation of LREMs and HREMs in the tree species

Stille et al., Brioschi et al. and Durães et al. stated that the roots preferentially absorb LREMs [32], [33], [34]. This may be related to the fact that LREMs are much more mobile in soil than HREMs and amplified by the greater stability of disintegrated HREMs complexes in soil, so that roots absorb free ions more easily [33]. In general, plant stems and leaves are rich in LREMs [33], [34]. HREMs are transported with the process of transpiration of the plant, leading to changes in parts of the stem [35].

The XRF results for the investigated samples also indicated the presence of some metals considered rare (Se, Ga, Re, At, In), but also large amounts of Al, Si and Ti, as seen in Table 3.

Table 3. Results obtained from XRF analysis of compounds containing other chemical elements

Plant species	**Sample code**	**Ash, (g)**	**Mineral type**	**Mineral conc. (%)**	**Mineral mass (g)**	**Metal weight (mg)**
Populus nigra L.	1	0.0542	Al_2O_3	0.5983	0.0324	17.2
Populus nigra L.	1	0.0542	SiO_2	14.3719	0.7790	370.3
Populus nigra L.	1	0.0542	TiO_2	2.9247	0.1585	95.1
Populus nigra L.	1	0.0542	In_2O_3	2.3735	0.1286	106.4
Aesculus hippocastanum L.	2	0.0512	Al_2O_3	0.6712	0.0344	18.2
Aesculus hippocastanum L.	2	0.0512	SiO_2	9.3806	0.4803	228.3
Aesculus hippocastanum L.	2	0.0512	Ga_2O_3	0.2509	0.0128	9.6
Aesculus hippocastanum L.	2	0.0512	SeO_2	0.3018	0.0155	11.0
Aesculus hippocastanum L.	2	0.0512	ReO_2	0.5400	0.0276	23.6
Populus x *canadensis* M.	4	0.0552	Al_2O_3	0.3459	0.0191	10.1
Populus x *canadensis* M.	4	0.0552	SiO_2	7.4023	0.4086	194.3
Fraxinus excelsior L.	5	0.0507	SiO_2	2.4974	0.1266	60.2
Fraxinus excelsior L.	5	0.0507	TiO_2	8.9319	0.4528	271.7
Fraxinus excelsior L.	5	0.0507	At	1.1337	0.0575	120.7
Populus tremula L.	6	0.0288	Al_2O_3	0.2823	0.0081	4.3
Populus tremula L.	6	0.0288	SiO_2	6.0844	0.1752	83.3
Populus tremula L.	6	0.0288	SeO_2	0.6954	0.0200	14.3
Betula pendula Roth	7	0.0527	SiO_2	2.4572	0.1295	61.6
Betula pendula Roth	7	0.0527	SeO_2	1.3383	0.0705	50.2

Although the specie *Aesculus hippocastanum* L. accumulated the highest number of elements, it is observed that the largest quantity was accumulated by *Populus nigra* L. (Figure 4).

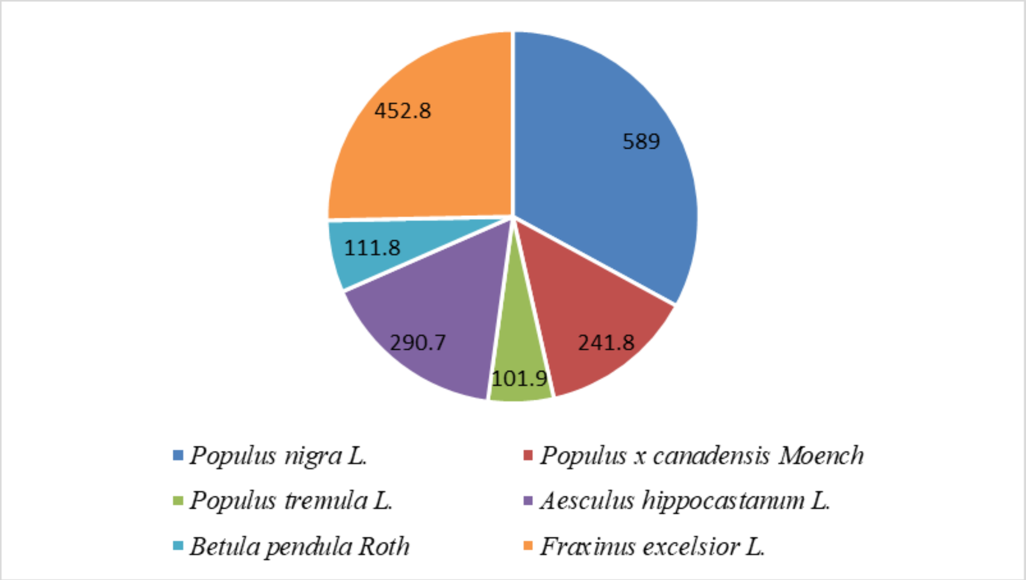

Fig. 4. Bioaccumulation of Al, Si, Ti, Se, Ga, Re, At, In in perennial plants (mg/kg dry mass).

All six samples of the investigated trees accumulated Si (998 mg/kg), although this is not an essential element for plant growth. The species *Populus nigra* L. and *Aesculus hippocastanum* L. have accumulated silicon (Si) in quantities of 370.3 mg/kg dry biomass, respectively 228.3 mg/kg dry biomass. Epstein et al. showed that plants that were not treated with the addition of silicon showed a weaker structure and abnormalities of growth, development, reproduction, they were more susceptible to stressors and diseases [36]. OSHA (The Occupational Safety and Health Administration) has set a silicon exposure limit of 15 mg/m^3, i.e. approximately 13.05 mg/kg. NIOSH (The National Institute for Occupational Safety and Health) recommends for silicon an exposure limit of 10 mg/m^3, i.e. approximately 8.7 mg/kg. Inhalation of silicon crystals leads to silicosis, an occupational lung disease.

All three species of poplar and chestnut accumulated aluminum (see Figure 5), but at values lower than 150 mg/kg dry biomass, which does not pose a risk to environmental and human health.

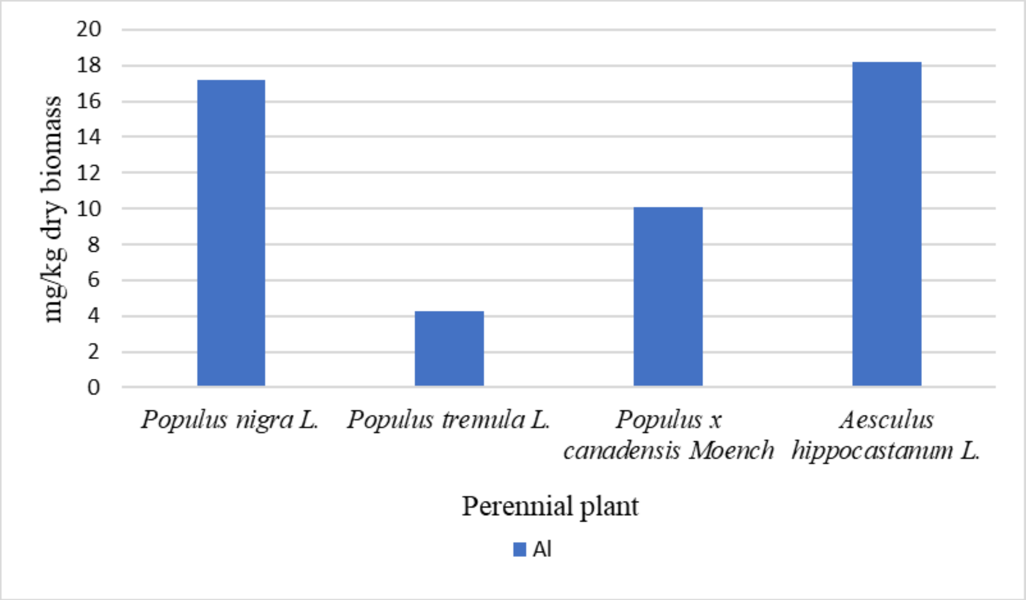

Fig. 5. Aluminium bioaccumulation in poplar and chestnut species.

Hutchinson and Chenery define Al-accumulating plants as plants that accumulate amounts higher than 1000 mg Al/kg dry mass [37], [38], while non-accumulating plants accumulate amounts less than 200 mg Al/kg dry mass [39]. Therefore, from the results of our study it can be stated that the analysed species are not adequate bioindicator plants to retain aluminium. For example, in the study carried out by Stan et al. amounts of approximately 6349 mg Al/kg dry biomass were obtained on some mosses samples collected from the northeastern part of Transylvania [40].

The experimental results also indicated that a large amount of titanium (Ti) was accumulated in the species *Fraxinus excelsior* L. (271.7 mg /kg dry biomass). Berrow and Cook et al. estimates that in the case of titanium, concentrations higher than 10 mg Ti / kg dry biomass in plant samples indicate a real soil pollution because the concentrations of Ti in the soil are much higher than those in plants [41], [42].

The perennial species *Populus tremula* L., *Aesculus hippocastanum* L., *Betula pendula* Roth and *Fraxinus excelsior* L. accumulated the five metals considered rare on Earth (Se, Ga, Re, In, At), in the largest amount being detected At, of 120.7 mg/kg dry biomass.

4. Conclusions

Air pollution is one of the main environmental problems associated with urbanization. The increasingly use of the rare-earth metals in various industries have been growing environmental concerns and social conflicts surrounding rare-earth minerals exploiting. Apart from their environmental and social impact, REMs may pose a risk to human health, particularly through their bioaccumulation in brain and bones.

Experimental research on the assessment of some light and heavy rare-earth metals bioaccumulation into six urban trees species used as bioindicators has led to the following conclusions:

- In the samples of investigated plants (*Populus nigra* L., *Populus tremula* L., *Populus x canadensis* Moench, *Betula pendula* Roth, *Aesculus hippocastanum* L., *Fraxinus excelsior* L.) 6 types of rare metals accumulated (Tb, Tm, Y, Dy, Eu, La); up to 2 rare metals have been detected in each species, except *Betula pendula* Roth;
- The highest value of the rare-earth metals accumulation index (REMs-AI) was recorded in *Populus tremula* L., approximately 10 times higher than in *Aesculus hippocastanum* L.; there has been recorded an excessive accumulation of Eu and La, but also traces of Y that could be attributed to the 1986 Chernobyl nuclear accident;
- The amounts of REMs vary from one species to another with values between 38.6-458.3 mg / kg dry mass, but the light rare-earth metals (La, Eu) were accumulated in quantities 3 times higher than the heavy rare-earth metals;
- In addition to the presence of rare-earth metals, an excessive accumulation of Si and Ti was recorded; Al was found in a concentration lower than the maximum allowed threshold.

This preliminary research proved that REMs bioaccumulation is species-specific. Some tree species can be used as good bioindicators to monitor air quality and the level of pollution generated by anthropogenic activities.

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