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BIOCONCENTRATION OF MERCURY AND HEAVY METALS BY THE BARK OF MAPLE-LEAF PLANE TREE

BIOKONCENTRACJA RTĘCI I METALI CIĘŻKICH PRZEZ KORĘ PLATANA KLONOLISTNEGO

Abstract: Continuous civilization progress, urbanization, and growing level of industrialization cause the fact that the contents of mercury and heavy metals in the natural environment is increasing, posing a threat to proper ontogenesis of all living organisms. Thus it is justified to monitor and control the accumulation of the above-mentioned elements in the environment. The main goal of our research was to determine whether maple-leaf plane tree (*Platanus x acerifolia*) may be used as a bioindicator of the air pollutants. This tree may be found all across Central Europe, it is quite resistant to different environment pollutions, and, what is very important, it sheds the bark every autumn. The research covered a determination of the analytical procedure capable of quantitive analysis of the contents of some given heavy metals: copper, zinc, iron, mercury and sulfur. The results and correctness of the procedure of the preparation of the bark samples for the analysis were confirmed by the research of a certified material (BCR-062 Olive leaves). Particular attention was put to the influence of the separated stages of the sample preparation (washing, drying, grinding down), especially for the mercury analysis due to the fact that this element is characterized by high volatility. To broaden the analysis, the samples were taken from different parts of the trees: limbs, trunks, and roots, as well as from different places, such as high-traffic streets, parks, and from different cities of Poland and Europe. Total mercury contents were measured by means of automatic Mercury Analyzer MA-2. The quantification determination of the transient-metal ions was performed on a emission spectrometer with inductively coupled plasma VARIAN VISTA-MPX.

Keywords: mercury, heavy metals, ICP-OES

Mercury, among other chemical elements, stands out from very high level of chemical and biological activity [1]. This element is very toxic, moreover, it is not subjected to biodegradation [2]. The toxicity of mercury is strongly correlated with its presence form, while the exposure depends on the way this element gets to the organisms. The emission of mercury to the atmosphere may be a result of some natural geochemical processes, biological methylation, as well human activities. Basic source of environmental-pollution mercury, being a result of human activities, is related with burning of the crude oil and coal, some smelting processes, battery and fluorescent-lamp production, and burning of waste materials [3-5]. Agriculture also participates in the pollution of nature environment by means of mercury - its derivatives are used for the production of seed grounds and some plant-protection preparations [1, 6]. For the non-industrial areas, elemental mercury dominates (98%) in comparison with mercury(II) in the aerosol and gaseous forms [7]. Small amount of mercury in the atmosphere is of organic nature, such as dimethylmercury and monomethyl mercury. Once emitted to the atmosphere as either bonded with some compounds, or as a vapour, mercury may be transported with the wind at a high distance. Mercury vapour is usually bonded by atmospheric dust, which in turn may be settled at the surface of the soil, water, and plants, polluting them. Mercury is quite easily absorbed by the plants (mainly the roots - 95%), also from the air.

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Recently, in European Union the emission of mercury considerably lowered; however, the concentration of this element in the environment still remains high. The report for the European Commission and Parliament in Brussels in the year 2005 pointed out an important issue for Poland as a leader in the liberation of mercury as a result of coal burning. Thus, it is appropriate to monitor and to control the accumulation of mercury in the natural environment in Poland and across Europe.

This work is devoted to the determination of total concentration of mercury and some heavy metals in the bark of the maple-leaf plane tree. For many years the bark of trees is a target for many researches on the elimination of pollution aspects related with heavy metals and organic compounds to be present in the air, in water solutions and sewage. As reported in the literature, so far the research was concentrated on such trees as: eucalyptus - *Eucalyptus camaldulensis* [8], guava - *Psydium guajawa* [9], pine tree [10], oak, fir tree, and spruce European tree [11, 12]. The main goal of the work was to determine whether maple-leaf plane tree (*Platanus x acerofolia*) may be used as an effective bio-indicator of the air pollution. This tree is to be found across almost all Middle Europe, is quite resistant to the pollution, and it throws down the bark every autumn and winter. Our research was concentrated on the determination of an analytical procedure capable of quantitive analysis of contents of such heavy metals, as copper, zinc, iron, manganese, mercury and, in addition, sulfur.

The results obtained as well as the accuracy of the proposed procedure of the preparation of the bark samples for the analysis was verified by the research on a certified material (BCR-062 Olive leaves). Particular attention was put on the influence of the stages of sample preparation (washing, drying, grinding, etc.), especially for such volatile element as mercury. In addition, the samples were (1) taken from different parts of a tree: branches, the trunk, and roots, (2) collected at different places (heavy-traffic streets, parks), and (3) in different cities and countries (Poland, Europe). Total concentration of mercury was determined by means of automatic mercury analyser Merkury Analyzer MA-2. The other above-mentioned heavy metals we determined by means of emission spectrometer with inductively-coupled plasma VISTA - MPX (VARIAN).

Reagents and methods

Sample preparation

- Sample collection

The samples of the bark of maple-leaf plane tree were collected from May to October 2008. The choice of the collection places was dictated by a differentiation of the places, from cities (Poland: Poznan, Kornik, Miedzyzdroje, Sopot, Europe: Vienna, Berlin, Padova, Rome, Slovakia - Tatrzanske Lomnice), to green areas such as parks. The samples were taken at the approximate height of 1 meter above the ground level.

- Preparation of the samples for the analysis

Samples of the bark were purified from the lichen by means of a ceramic knife. Next, the samples were cleaned by a tap water and further deionized water. Next, the bark was subjected to drying at the temperature 50°C, and grinded in an agate mortar. The grinded sample was drying till solid state at the temperature 110°C (approximately during 3 hours).

- Determination of total concentration of mercury

To determine total concentration of mercury, the method of cold vapur generation CV AAS was applied, by means of the automatic mercury analyzer MA-2. The determination procedure was composed of the following steps:

- Determination of concentration of metals (Cu, Fe, Mn, S, Zn)

Once the bark was prepared according to the above-described procedure, the samples were mineralized by means of the microwave mineralizer MDS-2000. The mineralization was performed inside Teflon bombs, in a mixture of 65% HNO_3 + H_2O_2 (5 : 2, 10 cm^3), at PSI 60 and POWER 40. After the mineralization the samples were put quantively to the 25 cm^3 flasks, supplemented by distilled water, and used for the determination of the above-mentioned heavy metals. The analysis was performed by means of the emission spectrometer with inductively coupled plasma ICP-MS of VARIAN company.

- Testing the quality of the determination method

To inspect the quality of the measurement, reference material BCR®-062 Olive leaves (*Olea europaea*) was applied. The determination of mercury concentration in the reference material was performed at the beginning and at the end of each experiment series. The certified concentration of mercury in the reference material was equal to 0.28 ± 0.02 mg · kg^{-1}. The measured (according to the above-described method) concentration was exactly 0.28 ± 0.01 mg · kg^{-1}. The certified concentration of copper in the reference material was equal to 46.6 ± 1.8 mg · kg^{-1}, manganese - 57.0 ± 2.4 mg · kg^{-1}, and zinc - 16.0 ± 0.7 mg · kg^{-1}, while the measured values for these metals 46.2 ± 0.5 mg · kg^{-1}, 56.8 ± 0.4 mg · kg^{-1}, and 15.8 ± 0.5 mg · kg^{-1}, respectively.

Results and discussion

The characteristics issue of the maple-leaf plane tree is related with shedding of the bark every year. Such a bark was inspected in our research, to determine the concentration of mercury and other elements, such as copper, iron, manganese, zinc and sulfur.

Table 1

Concentration of the metals under study [ppm] in the bark of maple-leaf plane tree, at some localization in Poland

Place	Concentration [ppm]					
	Hg	Cu	Fe	Mn	Zn	S
Miedzyzdroje 1	0.084 ± 0.010	4.1	84.5	12.1	9.0	700.7
Miedzyzdroje 2	0.062 ± 0.008	2.5	21.0	6.1	3.2	765.0
Sopot	0.065 ± 0.004	5.9	64.9	15.8	11.9	670.8
Kornik	0.14 ± 0.03	3.3	31.9	23.8	4.4	730.4
Poznan:						
PUE park 1*	0.063 ± 0.004	2.9	49.6	4.4	5.7	843.3
PUE park 2*	0.049 ± 0.005	2.1	31.4	4.4	2.2	592.2
Niepodleglosci Str. 1	0.13 ± 0.02	2.7	39.6	12.7	21.1	523.1
Niepodleglosci Str. 2	0.12 ± 0.02	1.7	12.2	4.5	7.5	494.1
Niepodleglosci Str. 3	0.14 ± 0.02	2.5	25.1	5.4	3.6	621.4
Niepodleglosci Str. 4	0.09 ± 0.04	8.6	156.9	19.9	17.6	584.8
Sniadeckich Str.	0.16 ± 0.03	10.0	222.9	19.1	24.4	1067.2

*Parks near Poznan University of Economics

The samples were taken from different parts of the tree: branches, trunk, and roots, as well as at different places across Poland and Europe. In Table 1 some results of determination of mercury and other heavy metals are given, for the samples collected in Poland, while in Table 2 - for the samples collected across Europe.

Table 2

Concentration of the metals under study [ppm] in the bark of maple-leaf plane tree, at some localization in Europe

Place	Concentration [ppm]					
	Hg	Cu	Fe	Mn	Zn	S
Berlin	0.063 ± 0.003	4.6	39.8	25.1	16.5	1016.6
Padova	0.086 ± 0.001	16.5	128.8	17.2	14.7	1075.5
Rome	0.067 ± 0.005	12.6	171.3	14.6	9.5	1345.3
Vienna	0.067 ± 0.004	9.0	80.8	24.7	21.8	920.6
Slovakia - Tatrzanske Lomnice	0.078 ± 0.006	4.5	46.0	201.7	52.0	485.9

As it may be deduced from an analysis of the results presented in Table 1, the concentration of the metals is different for different samples. This situation may be caused by the fact that the samples were collected from the places of different nature, such as the streets or the green areas (parks). The highest concentration of all the elements under study was detected at Sniadeckich Str. in Poznan. This place is located very close to the city center, moreover, Faculty of Chemistry and a big hospital are nearby. The lowest concentration was detected for a park near Poznan University of Economics (PUE) - this place is quite separated from the city traffic. Sample No. 4 was taken from a young tree at Niepodleglosci Str., Poznan. In this case large concentration was detected of such elements as copper, zinc and iron. These metals are responsible for proper ontogenesis, growth, and metabolism of the tree, as well as for photosynthesis process. High concentration levels are probably caused by intensive growth of this young tree. At the seaside, concentration levels of mercury are very similar (0.06÷0.08 ppm). Such low concentration is probably related with low emission to the atmosphere, and strong winds to and from the sea, forcing the replacement of the pollutants at a higher distance.

As it may be deduced from an analysis of the results presented in Table 1, the concentration of the metals is from 0.06 to 0.08 ppm. The highest concentration was detected in Padova (Italy) - this fact is probably related with a presence of large mercury deposits nearby. The concentration of manganese for the sample from Slovakia (Tatrzanske Lomnice) is pretty high - 201.7 ppm. It may be justified by the presence of large deposits of the ore of this element in this region, as well as related industry. Unfortunately, this area is poor in pyrite deposits, thus low concentration levels determined for sulfur and iron, in comparison with other European cities. On the contrary, Rome (Italy) area is reach in pyrite deposits, thus the concentration levels of sulfur and iron are high. In the bark collected in Berlin (Germany), lowest concentration levels were detected for such elements as mangan, iron, zinc and sulfur. Probably, the soil there was drain of its nutrients, these elements included. It proofs the fact that the concentration levels of the metals in the bark are related with the corresponding levels for the soil. Heavy metals are cumulated by the vascular plants, however, in a smaller amounts than the moss.

In Table 3 some results are given of the analysis of concentration of heavy metals in different parts of the maple-leaf plane tree (branches, trunk, roots). The samples were taken at Sniadeckich Str., Poznan, Poland.

Table 3

Concentration of the metals under study [ppm] in the parts of the plane tree

Maple-leaf plane tree	Concentration [ppm]					
	Hg	**Cu**	**Fe**	**Mn**	**Zn**	**S**
branches	0.26 ± 0.03	6.5	106.3	17.4	9.9	870.1
trunk	0.16 ± 0.03	10.0	222.9	19.1	24.4	1067.2
roots	0.21 ± 0.06	2.0	264.3	14.0	14.5	727.2

As it may be deduced, the highest concentration of the mercury was detected in the branches, while the lowest - in the trunk. It is probably caused by the fact that the adsorption of the pollutants by the bark is conditioned by wet and dry deposition, which in turn is conditioned by the size of the tree crown. Thus, the pollutants carried by the wind are mainly deposited at the branches and leaves. The high concentration of mercury in the roots may be explained by the fact that the pollutants are present in the soil, as a result of the contact with the rain water, and the city-polluted atmosphere.

Conclusions

While analyzing the bark of the maple-leaf plane tree, one may uncover important information about a level of degradation of the natural environment, from the moment of the development of the new bark, to its shedding. What is particularly important is the procedure of sample preparation, as improper treatment of the samples may significantly rise the detected concentration levels. By means of the proposed method, while undertaking the research on plant samples we are able to determine the contents of the pollutants not only at the plant surface, but also inside the plants.

To determine the pollution level one has to collect the samples from different, well-matched places, taking into account not only the localization of the place, but also tree part. One must note that some parts of the tree are subjected to decomposition, sometimes fast.

According to the samples we collected for this research, the highest concentration of the pollutants is usually determined for the crowded city streets, while the lowest - for the parks, even inside urban area.

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BIOKONCENTRACJA RTĘCI I METALI CIĘŻKICH PRZEZ KORĘ PLATANA KLONOLISTNEGO

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Abstrakt: Ciągły rozwój cywilizacyjny, urbanizacja, postępujące uprzemysłowienie sprawiają, iż zawartość rtęci i metali ciężkich w środowisku naturalnym wzrasta i stwarza zagrożenie dla prawidłowego rozwoju wszystkich organizmów. Wydaje się więc celowe, aby monitorować i kontrolować akumulowanie wspomnianych pierwiastków w naszym środowisku. Celem badań było określenie, czy platan klonolistny (*Platanus x acerifolia*) może służyć jako bioindykator zanieczyszczeń powietrza. Drzewo to występuje prawie w całej Europie Środkowej, jest stosunkowo odporne na zanieczyszczenia środowiska, a jego cechą charakterystyczną jest zrzucanie kory. Przeprowadzone badania obejmowały opracowanie procedury analitycznej pozwalającej na analizę ilościową zawartości wytypowanych metali ciężkich: miedzi, cynku, żelaza, manganu, rtęci oraz dodatkowo siarki. Wyniki i poprawność stosowanej procedury przygotowania próbek kory do analizy potwierdzono badaniami materiału certyfikowanego (BCR-062 Olive leaves). Zwrócono szczególną uwagę na wpływ poszczególnych etapów przygotowania próbek (mycie, suszenie, rozdrabnianie itd.), co zwłaszcza w przypadku rtęci ma bardzo duże znaczenie z uwagi na jej dużą lotność. Ponadto przebadano próbki pochodzące z różnych części drzewa: konary, pień i korzenie. Kolejną zmienną były miejsca pobrania próbek, kora drzew rosnących przy ruchliwych ulicach, w parkach, pobrane w różnych miastach Polski i Europy. Całkowitą zawartość rtęci oznaczono, wykorzystując automatyczny analizator rtęci Merkury Analyzer MA-2. Pozostałe metale ciężkie oznaczono na spektrometrze emisyjnym z indukcyjnie sprzężoną plazmą VISTA - MPX firmy VARIAN.

Słowa kluczowe: rtęć i metale ciężkie, ICP-OES