THE HEAVY METALS ACCUMULATION IN FOLIAR TISSUE OF ORNAMENTAL TREES FROM AGGLOMERATED URBAN SPACES. A CASE STUDY: Cu AND Ni ACCUMULATION IN *Aesculus hippocastanum* L. LEAVES OF TREES FROM CLUJ-NAPOCA

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Abstract. *In the surrounding air, metals and the compounds they form are mainly found as constituents of the particles (particulate matter). The copper pollution of the environmental air, like other heavy metals air pollution, has as source anthropogenic, and also natural sources. In order to perform an assessment of the heavy metals air pollution on health effects, one have to know about the metallic species that are emitted into the environmental air, and/or about the compounds that are involved in the formation of the main metallic components. One of the most important copper air pollution come from dust resulted from the mining activity. Nickel may form a series of compounds that can occur in different oxidation states, but the divalent ions are considered to be of greatest importance whatever inorganic or organic compounds, where they are encountered. The purpose of the present study is to quantify the accumulations of copper and nickel in the foliage of chestnut trees, in the municipality of Cluj-Napoca, in order to quantify the degree of pollution with heavy metals in areas with different vulnerabilities to this type of pollution. The experiment was conducted from April 1, 2019 up to September 30, 2019, in the municipality of Cluj-Napoca. The leaf tissue of the chestnut tree species constituted the biological material taken into account during the experiments. In the field, the observations were made in 4 experimental points. Regarding the accumulation of Cu and Ni in the leaf tissue of the Aesculus hippocastanum L. trees taken in the study, we identified the highest means corresponding to the experimental location no. 4 and minimum corresponding to the chestnut trees located in the experimental location no. 1. The increase of Cu and Ni accumulations is variable, being favored by the climatic factors, in different degrees of intensity, depending on the characteristics of the experimental locations.*

Keywords*: environment, heavy metals, pollution.*

INTRODUCTION

Unlike specific gaseous compounds, such as, for example, benzene or carbon monoxide, the assessment of metalloid and/or metal compounds in environmental air is not easy to perform because there are a series of different metallic species that have different toxicity, which may vary in a large range, but also more or less carcinogenic potency (BRÉDA AND BADEAU, 2008; LIU ET AL., 2019; TOMOHIRO AND MASAAKI, 2002; WANG, 2012). For this reason, in order to perform an assessment of the heavy metals air pollution on health effects, one have to know about the metallic species that are emitted into the environmental air, and/or about the compounds that are involved in the formation of the main metallic components (LEPP, 2012; SPOKES AND JICKELLS, 1995).

In the surrounding air, metals and the compounds they form are mainly found as constituents of the particles (particulate matter). They may be present in structures as spinels, which are non-stoichiometric, non-soluble mixture phases, or in salts that are soluble ionic structures. Heavy metals may also be found in gaseous phase (where the form organometallic compounds), and in this phase cannot be part of particulate matter (CAI ET AL., 2017; VENTRURA ET AL., 2017).

The copper pollution of the environmental air, like other heavy metals air pollution, has as source anthropogenic, and also natural sources. One of the most important copper air pollution come from dust resulted from the mining activity (HAN ET AL., 2007; KHAN ET AL., 2008; TASIĆ ET AL., 2010). Another source of copper pollution is the use of the fossil fuels, and also other industrial processes (as electronic manufacturing) that have as result the air emissions of gases that contain besides other pollutants, also copper (LOPEZ ET AL., 2007). Similarly with nickel, copper in air may be found as pollutant as constituent of particulate matters (OPINCARIU ET AL., 2018).

Nickel (Ni) is a metal that has a color, which may be considered from white to silver. Nickel may form a series of compounds that can occur in different oxidation states, but the divalent ions are considered to be of greatest importance whatever inorganic or organic compounds, where they are encountered (SCHMIDT AND ANDREN, 1990). The trivalent nickel ions are usually generated by redox reactions that occur in a specific cell. Because the nickel release may be the result of many sources, the nickel occurrence in the surrounding air can show considerable variations. In areas considered clean, the nickel levels in environmental air range within the interval 0.38-0.62 ng/m^3, while around factories, the nickel concentrations in air may reach the level of 124 ng/m^3. In some countries from Europe, in unpolluted areas levels around about 1 ng/m^3 nickel may be encountered, while at some distance from factories' furnaces (about 5 km) nickel levels of 5 ng/m^3 may be reported (SALTZMAN, 1985).

The purpose of the present study is to quantify the accumulations of copper and nickel in the foliage of chestnut trees, in the municipality of Cluj-Napoca, in order to quantify the degree of pollution with heavy metals in areas with different vulnerabilities to this type of pollution.

MATERIAL AND METHODS

The experiment was conducted from April 1, 2019 up to September 30, 2019, in the municipality of Cluj-Napoca. The leaf tissue of the chestnut tree species constituted the biological material taken into account during the experiments. In the field, the observations were made in 4 experimental points, in which there are ornamental trees belonging to the species *Aesculus hippocastanum* L., respectively: 1, in the vicinity of the Air quality monitoring station located on Aurel Vlaicu Street; 2, in the vicinity of the Suburban type air quality monitoring station located on Boulevard 1 December 1918; 3, in the vicinity of the urban air quality monitoring station located on Boulevard 1 December 1918 and 4, in the UASVM Campus Cluj-Napoca. Air quality monitoring stations are located by the Cluj Med Protection Agency. The samples were harvested twice a week during the experimental period. Immediately after harvesting, the leaf tissue samples were transported to the UASVM Cluj-Napoca Environmental Quality Monitoring Laboratory.

The samples were processed as soon as their reception was performed, in order to determine the dry substance, by the gravimetric method.

For the quantification of Cu and Ni from the leaf tissue of the *Aesculus hippocastanum* L. trees, monitored, the atomic absorption spectrometer (AAS) was used, respectively a Perkin-Elmer atomic absorption spectrometer (Perkin-Elmer, USA) with flame and graphite furnace.

RESULTS AND DISCUSSIONS

Regarding the accumulation of Cu in the leaf tissue of the *Aesculus hippocastanum* L. trees taken in the study, we identified means in the range 8.25 mg/kg corresponding to the experimental location no. 4 for the UASVM Campus Cluj-Napoca and 13.29 mg/kg corresponding to the chestnut trees located in the experimental location no. 1, from the proximity of the Air Quality Monitoring Station of EPA Cluj, of traffic type). Concentration mean in chestnut tree foliage tissue are representative. This representativeness is conferred by the values of the variability of the concentrations Cu in the leaf tissue of the chestnut trees, located below and highlighted by the coefficients of variation, with values below the threshold of 30%, are in the range CV = 18.22%, corresponding to the experimental location no. 3 and CV = 22.96%, corresponding to the experimental location no. 2 (Table 1).

Table 1

The basic statistics for the Cu concentration in foliar tissue of the *Aesculus hippocastanum* L. species, by analyzed experimental locations, by experimental period April – September 2019 (mg/kg leaf dry matter)

Experimental location	N	X	Minimum	Maximum	s	CV, %
1	120	13.29	10.00	16.00	2.45	18.43
2	120	10.58	7.00	12.00	2.43	22.96
3	120	9.11	8.00	10.00	1.66	18.22
4	120	8.25	5.00	12.00	1.71	20.72

The study of the differences and the significance of the differences between the Cu mean concentrations in the chestnut leaf tissue between the analyzed experimental sites, shows that the statistically assured differences at the 1% significance threshold are reported between the experimental location 1 and other two, respectively 3 and 4, in favor of the values of the Cu concentration, in the chestnut leaf tissue from the experimental location no. 1 (Table 2). These results show a higher concentration recorded in the chestnut trees located in the experimental location no. 1, from the proximity of the monitoring station of the air quality of traffic type and implicitly that an intense traffic leads to increased emissions of Cu in the ambient air.

Table 2

The differences and the significance of differences between the Cu concentrations in foliar tissue of the *Aesculus hippocastanum* L. species, by analyzed experimental locations, by experimental period April – September 2019 (mg/kg leaf dry matter)

Differences		DF	p
D1 – 2	2,71 [a]	238	0,143
D1 – 3	4,18 [c]	238	0,006
D1 – 4	4,98 [c]	238	0,002
D2 – 3	1.47 [a]	238	0,188
D2 – 4	2.27 [a]	238	0,112
D3 – 4	0,86 [a]	238	0,531

a – p > 0,05; c – p < 0,01.

Regarding the accumulation of Ni in the leaf tissue of the *Aesculus hippocastanum* L. arboretum taken in the study, means in the range 0.99 mg/kg were identified corresponding to the experimental location no. 4 for the UASVM Campus Cluj-Napoca and 5.22 mg/kg corresponding to the chestnut trees located in the experimental location no. 2, from the proximity of the EPA Cluj suburban type air quality monitoring station. The means of Ni concentrations in the leaf tissue of chestnut trees are representative. This representativeness is conferred by the values of the variability of the Ni concentrations in the leaf tissue of the chestnut trees, located below and highlighted by the coefficients of variation, with values below the threshold of 30%, are in the range CV = 3.44%, corresponding to the experimental location no. 2 and CV = 14.59%, corresponding to the experimental location no. 1 (Table 3).

Table 3

The basic statistics for the Ni concentration in foliar tissue of the *Aesculus hippocastanum* L. species, by analyzed experimental locations, by experimental period April – September 2019 (mg/kg leaf dry matter)

Experimental location	N	X	Minimum	Maximum	s	CV, %
1	120	1.85	1.13	1.98	0.27	14.59
2	120	5.22	5.31	7.13	0.18	3.44
3	120	2.62	2.88	3.96	0.31	11.83
4	120	0.99	1.12	2.74	0.12	12.12

The study of the differences and the significance of the differences between the Ni concentrations in the chestnut leaf tissue between the experimental locations analyzed, shows that statistically assured differences at the 0.1% significance threshold are reported between locations (Table 4).

Table 4

The differences and the significance of differences between the Ni concentrations in foliar tissue of the *Aesculus hippocastanum* L. species, by analysed experimental locations, by experimental period April – September 2019 (mg/kg leaf dry matter)

Differences		DF	p
D1 – 2	-3,37 ^{d}	238	< 0,001
D1 – 3	-0,77 ^{c}	238	0,008
D1 – 4	0,86 ^{c}	238	0,005
D2 – 3	2,60 ^{d}	238	< 0,001
D2 – 4	4,23 ^{d}	238	< 0,001
D3 – 4	1,63 ^{d}	238	< 0,001

c – p < 0,01; d – p < 0,001.

CONCLUSIONS

Regarding the accumulation of Cu in the leaf tissue of the *Aesculus hippocastanum* L. trees taken in the study, we identified means in the range 8.25 mg/kg corresponding to the experimental location no. 4 and 13.29 mg/kg corresponding to the chestnut trees located in the experimental location no. 1. The increase of Cu accumulations is variable, being favored by the climatic factors, in different degrees of intensity, depending on the characteristics of the experimental locations.

The accumulation of Ni has a mean of 0.99 mg/kg corresponding to the experimental location no. 4 for the UASVM Campus Cluj-Napoca and 5.22 mg/kg corresponding to the chestnut trees located in the experimental location no. 2. The increase of Ni accumulations is variable, being favored by climatic factors, in varying degrees of intensity, depending on the characteristics of the experimental locations.

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