STUDY REGARDING THE CAPACITY OF QUANTIFYING POLLUTION WITH MACRONUTRIENTS (S, N) USING ORNAMENTAL TREES AS BIOMONITORS IN CLUJ-NAPOCA

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Abstract. *In present conditions, in which urban pollution generates many concerns at the level of international establishment involved in assuming decisions regarding Earths health, an important role is given for establishing and maintaining green areas located in cities. This presents a worthy health importance, especially when their presence involves the existence of ornamental trees, used frequently in urban spaces (chestnut, linden, pine) that can substantially contribute in improving air quality. Regarding the quantification of air quality influence upon physiological disease in trees, it was resorted to sample leaf tissue and / or needle from three species of ornamental trees, located in the proximity of two monitoring stations in Cluj-Napoca subjected to different intensity of pollution degrees, twice a week, during the experimental period April-September 2014-2015. In Tillia cordata, in the foliar tissue, weak correlations were found, positive between sulphur and nitrogen (R = +0.394, CLU-1; R = +0.312, CLU-4), implying that increased sulphur in foliar tissue leads to the increase of nitrogen for a proportion of total foliar tissue equal to related determination coefficients (15.5%; 9.7%). The results of the present research, demonstrate, in this way, that Tilia cordata has the biggest capacity of sulphur and nitrogen bioaccumulation, while in Pinus nigra, and Aesculus hippocastanum have the lowest capacities of sulphur and nitrogen bioaccumulation. Based on this results, we can recommend planting Tilia cordata species in urban areas where there is a risk of pollution caused by sulphur and nitrogen, due to its high capacity of monitoring air pollution in most of these macronutrients. Elements that give originality to this present research consists in the quantification and analysis of interactions between the sulphur and nitrogen content in leaf tissue / needle of tree species taken under study, through simple correlations between those two elements essential in the metabolism and intimate physiological mechanisms of vegetable tissue.*

Key words: *air quality, biomonitors, macronutrients, ornamental trees.*

INTRODUCTION

The air quality control is the process of the quantitative, qualitative and repetitive observation and measurement of the concentration of one or several air constituents. The data delivered by the monitoring network allow the calculation of the indicators of the air quality, identification of the polluted areas, comparisons with threshold values of air quality established by regulation and rapid measurements of fight against pollution and prevention of pollution. The placement of the network of surveillance of the air quality must be selected in a manner that it is possible to monitor the cumulated effect of industry, traffic, warming of houses, and commercial spaces (PROOROCU ET AL., 2008).

Atmospheric pollution represent, in present days, a major preoccupation in the urban environment. Different toxic gases, coarse and fine particulate matter, trace elements and heavy metals emitted from anthropogenic sources cause different impacts not only upon urban environment, but also upon human health and biotic communities. Among this anthropogenic sources, the way the land is used, is, in a certain way, responsible of atmospheric contamination (OROIAN ET AL., 2012).

Absorption and accumulation capacity of environmental toxicity in foliage, the advantage of an increased mass and easy disposal, makes it possible for plants to eliminate toxic substances through in situ phytoremediation, and, in consequence, to reduce the pollutants concentration in the urban environment. As such, greening by planting, whereby vegetation is used for removing, detoxifying and stabilizing persistent pollutants, represents a green and environmental friendly instrument for cleaning urban environment (RAO, 1985; SMITH, 1990).

MATERIAL AND METHODS

In order to quantify the influence of air quality upon physiological diseases in ornamental trees, we recourse to sampling leaf tissue and / or needle from 3 species of ornamental trees, located in the proximity of 2 monitoring stations in Cluj-Napoca county, subjected to sources of pollution of varying degrees of intensity. Foliage tissue samples were collected during the vegetation period (April-September, 2014, 2015), from the trees species selected at the level of each air quality monitoring stations from Cluj-Napoca (Environmental Protection National Agency Cluj, Environmental Reports, 2010-2015). Monitoring station CLU-1 is located in Mărăşti. Aurel Vlaicu Street and monitoring station CLU-4 is located in Mărăşti, Dâmboviţei Street in the precincts of EXPO TRANSILVANIA.

The biological material taken into consideration in order to quantify air quality, in the present study, consists from tree species used in urban spaces. This, corresponding to each of the monitoring stations CLU-1 (traffic) and CLU-4 (industrial), are: black pine (*Pinus nigra*), chestnut (*Aesculus hippocastanum*) and linden (*Tilia cordata*).

Physical materials necessary in order to realize the experimental study are represented by the mobile equipment necessary for the quantification of sulphur dioxide (SO_2) and nitrogen oxide (NOx) in air (Chemist 503 cell analyser), thermobalance („Precisa") for determination of dry matter of leaves / needles of studied trees and XRF spectrometer respectively Spectroradiometer Comet BLACK C-25.

After sampling (twice a week), leaf tissue and / or needle samples were labelled and transported to the Environmental and Plant Protection Laboratory of UASVM Cluj-Napoca. Here, were subjected to preliminary processing, in order to determinate dry matter. Thereby, quota/part of the fresh foliar tissue/needles samples were placed in the thermobalance and subsequently, after the analysis of the thermobalance display is recorded the percentage of dry matter substance. After drying, the samples were homogenized with an electric mill. .The content of foliar tissue in macronutrients (S, N) were determined in the Laboratory of the National Institute of Research-Development for Industrial Ecology, ECOIND, Bucharest. Statistical data processing was realised using STATISTICA v.8.0 programme for Windows. Mean, standard deviation, standard error of mean, variance and coefficient of variation were calculated at the 95% confidence interval.

RESULTS AND DISCUSSION

Taken into consideration the results of the present study, as average by two experimental years, 2014 and 2015, located in the proximity of monitoring station type traffic, CLU-1, the air quality, characterized in terms of the content in sulphur and nitrogen dioxide, is defined by a mean concentration of sulphur dioxide in air, of 8.20 $\mu g/m^3$ and a mean of nitrogen oxides of 75.50 $\mu g/m^3$. According to the coefficients of variability, 19.75% and 9.16%, respectively, the means are representative for the studied area (Table 1). For both SO_2

and NOx, the recorded means are under the hourly limit values for the protection of human health (350 µg/m^3 and respectively 200 µg/m^3), but for NOx, this mean exceeds the annual critical level for vegetation protection (30 µg/m^3).

Table 1

The mean and statistical indicators of the air SO_2 and NO_x concentrations (µg/m^3) quantified in traffic monitoring station CLU – 1, of the Cluj – Napoca municipality

Statistical indicator		SO_2 µg/m^3	NO_2 µg/m^3
n		106	106
Mean		**8.20**	**75.50**
The interval of confidence	+95%	7.04	70.55
	-95%	9.36	80.45
Variance		2.62	47.83
Standard deviation		1.62	6.92
Standard error of the mean		0.16	0.67
Coefficient of variability		19.75	9.16

The study of the S and N content in the needle, and foliar tissue, respectively of the analysed species, emphasizes same size order, having, in certain cases, even close values (Table 2, 3 and 4).

Table 2

The mean and statistical indicators S (ppm) and N (g/kg) in the needles tissue of the *Pinus nigra* specie, in traffic monitoring station CLU – 1, Cluj – Napoca

Statistical indicator		S ppm	N g/kg
n		106	106
Mean		**64.47**	**16.23**
The interval of confidence	+95%	61.48	14.90
	-95%	67.46	17.57
Variance		17.44	3.48
Standard deviation		4.18	1.86
Standard error of the mean		0.41	0.18
Coefficient of variability		6.48	11.49

Table 3

The mean and statistical indicators of, S (ppm) and N (g/kg) in the foliar tissue of the *Aesculus hippocastanum* specie, in traffic monitoring station CLU – 1, Cluj – Napoca

Statistical indicator		S ppm	N g/kg
n		106	106
Mean		**90.56**	**16,80**
The interval of confidence	+95%	85.98	15.43
	-95%	95.14	18.17
Variance		40.94	3.68
Standard deviation		6.40	1.92
Standard error of the mean		0.62	0.19
Coefficient of variability		7.07	11.42

The study of the interrelation between sulphur and nitrogen content in the foliar/acicular tissue of each analysed specie in the experimental site located in the proximity of the monitoring station CLU-1, emphasize a strong negative correlation (R = -0.781), in acicular tissue of *Pinus nigra*, which is applicable for 60.9% of the total needles of black pine. The level of nitrogen concentration increases, while the sulphur decreases, according to the regression line (Table 5).

Table 4

The mean and statistical indicators of S (ppm) and N (g/kg) in the foliar tissue of the *Tilia cordata* specie, in traffic monitoring station CLU – 1, Cluj – Napoca

Statistical indicator		S ppm	N g/kg
n		106	106
Mean		**84.77**	**20.80**
The interval of confidence	+95%	80.99	18.91
	-95%	88.55	22.69
Variance		27.92	7.01
Standard deviation		5.28	2.65
Standard error of the mean		0.51	0.26
Coefficient of variability		6.23	12.73

Table 5

The interaction between the foliar content of the S (ppm) and N (considered as bioindicators of the air quality

Specie	R	R^2	Regression line	p
Pinus nigra	-0.781	0.609	X = 77.312 – 0.155Y	0.198
Aesculus hippocastanum	-0.333	0.111	X = 71.882 – 0.111Y	0.346
Tillia cordata	+0.394	0.155	X = 47.639 + 0.448Y	0.402

Week correlations are recorded between the content of sulphur and nitrogen in the foliar tissues of *Aesculus hippocastanum* (R = -0.333) and of *Tilia cordata* (R = +0.394). In 11.1% of the total chestnut leafs located in the proximity of the monitoring station CLU-1, as the nitrogen concentration increases, the sulphur decreases and in 15.5% of the total linden leafs located in the same experimental site, the increase of nitrogen concentration entails and increase of sulphur concentration, as described by the regression lines (Table 5).

During the experimental period 2014 - 2015, in the experimental field located in the proximity of the monitoring station of industrial type, CLU-4, the means of the nitrogen oxide and sulphur dioxide are inferior to those located in CLU-1, being of 42.4 $\mu g/m^3$ and, 7.76 $\mu g/m^3$, respectively. The coefficient of variability is of 8.63% for NOx. These values demonstrate the homogeneity of values of the nitrogen oxide concentration, while, for SO_2, the value of the coefficient of variability is of 22.89%, suggesting a moderate homogeneity (Table 6).

Although this average values are inferior to the hourly limits for the protection of the human health, in the case of nitrogen oxide, the mean exceed the annual critical level for the vegetation protection (Table 6).

Table 6

The mean and statistical indicators of the air SO_2 and NO_x concentrations ($\mu g/m^3$) quantified in industrial monitoring station CLU – 4, of the Cluj – Napoca municipality

Statistical indicator		SO_2 $\mu g/m^3$	NO_2 $\mu g/m^3$
n		106	106
Mean		**7.76**	**42.40**
The interval of confidence	+95%	6.49	39.78
	-95%	9.03	45.02
Variance		3.15	13.38
Standard deviation		1.78	3.66
Standard error of the mean		0.17	0.36
Coefficient of variability		22.89	8.63

Sulphur concentration in foliar tissue of *Tillia cordata*, of 126.41 ppm, while in *Aesculus hippocastanum*, the sulphur concentration in foliar tissue is equal with 71.99 ppm. In the acicular tissue of *Pinus nigra* sulphur concentration is of 71.54 ppm (Tables 7, 8 and 9). Nitrogen concentration in foliar/acicular tissues of linden, chestnut and black pine are of the same size order.

There are recorded two exceptions, in *Tillia cordata*, where, in sulphur concentration, is identified a great variability of its content in the foliar tissue (CV=33.40%), which means that in this case the mean less representative. Also, concerning nitrogen, the variability equal with 17.01% indicates moderate homogeneity of its content in the foliar tissue of the linden located in the experimental field, but in this case, the mean is representative (Table 7).

Table 7

The mean and statistical indicators S (ppm) and N (g/kg) in the foliar tissue of the *Tilia cordata* specie, in industrial monitoring station CLU – 4, Cluj – Napoca

Statistical indicator		S ppm	N g/kg
n		106	106
Mean		**126.41**	**20.39**
The interval of confidence	+95%	96.20	17.91
	-95%	156.61	22.87
Variance		1782.42	12.03
Standard deviation		42.22	3.47
Standard error of the mean		4.09	0.33
Coefficient of variability		33.40	17.01

Table 8

The mean and statistical indicators of S (ppm) and N (g/kg) in the foliar tissue of the *Aesculus hippocastanum* specie, in industrial monitoring station CLU – 4, Cluj – Napoca

Statistical indicator		S ppm	N g/kg
n		106	106
Mean		**71.99**	**16.58**
The interval of confidence	+95%	66.60	15.58
	-95%	77.37	17.58
Variance		56.68	1.95
Standard deviation		7.53	1.40
Standard error of the mean		0.73	0.13
Coefficient of variability		10.46	8.42

Table 9

The mean and statistical indicators of S (ppm) and N (g/kg) in the needle tissue of the *Pinus nigra* specie, in industrial monitoring station CLU – 4, Cluj – Napoca

Statistical indicator		S ppm	N g/kg
n		106	106
Mean		**71.54**	**13.84**
The interval of confidence	+95%	65.33	12.63
	-95%	77.75	15.05
Variance		75.36	2.85
Standard deviation		8.68	1.69
Standard error of the mean		0.84	0.16
Coefficient of variability		12.13	12.20

Interactions between sulphur and nitrogen content in the foliar/acicular tissues of the studied trees (Table 10) are weak and negative in *Aesculus hippocastanum* (R = -0.245) and strong negative in *Pinus nigra* (R = -0.888). According to the coefficients of determination, as the nitrogen concentration increases, the sulphur decreases, in 5.3% of the total leafs of *Aesculus hippocastanum* and 78.8% of total needles of *Pinus nigra*, in a manner described by the regression lines. Between the sulphur and nitrogen content in foliar tissue of *Tilia cordata (*R = +0.312), in 9.7% of the total leafs, the increase of nitrogen concentration entails an increase of sulphur concentration, as described by the regression line (Table 10).

Table 10

The interaction between the foliar content of the S (ppm) and N (g/kg) considered as bioindicators of the air quality

Specie	R	R^2	Regression line	p
Tillia cordata	+0.312	0.097	X = 87.835 + 0.332Y	0.199
Aesculus hippocastanum	-0.231	0.053	X = 53.419 – 0.113Y	0.113
Pinus nigra	-0.888	0.788	X = 71.216 – 0.283Y	0.073

By the experimental period April-September, 2014 - 2015, in the experimental field located in the proximity of the monitoring station type urban CLU-1, were recorded the highest values of SO_2 concentrations SO_2 (8.2 μg/m^3) and NO_x (75.5 μg/m^3), while minimal values were recorded in the experimental area located in the proximity of the monitoring station CLU-4, of industrial type, being of 7.76 μg/m^3 for SO_2 and 42.4 μg/m^3 for NO_x , respectively (Fig. 1).

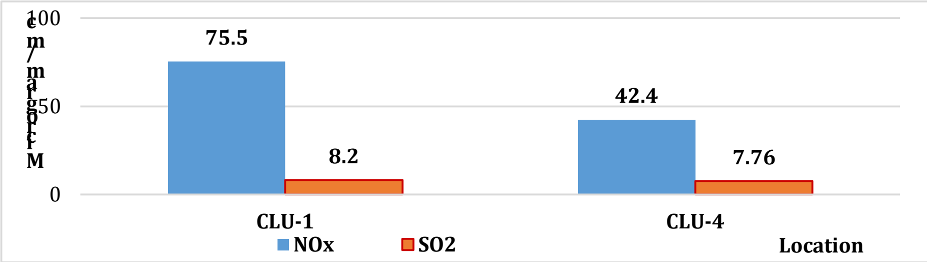

Fig. 1. The evolution of SO_2 and NOx air concentrations, in experimental sites localized in Cluj – Napoca, 2014 - 2015

In *Pinus nigra*, sulphur concentration was of 64.47 ppm in the experimental field located in the proximity of the type traffic monitoring station CLU-1 and 71.54 ppm in the experimental area located in CLU-4 (Fig. 2), where are reported the lowest SO_2 concentrations in air.

In *Pinus nigra*, it was recorded the lowest value of nitrogen concentration, y 13.84 g/kg respectively, in the experimental area located in the proximity of the monitoring station CLU-4 (Fig. 3), where is reported the lowest concentration of NOx in air (Fig. 1).

In the experimental area located in the proximity of the monitoring station CLU-1, of traffic type, the concentration of NOx in air is of 16.23 g/kg. In the same areas, one may note the *Aesculus hippocastanum* species, were it has been identified low nitrogen concentrations, 16.8 g/kg and 16.58 g/kg, respectively (Fig. 3).

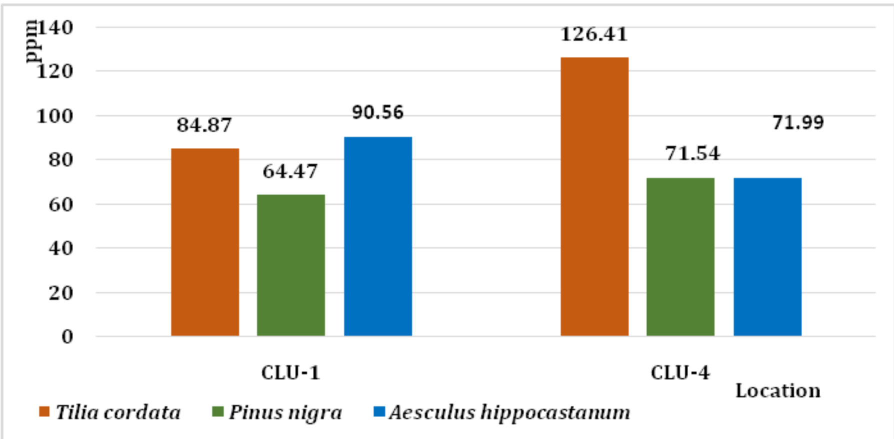

Fig. 2. The evolution sulphur concentrations, in foliar tissue of *Tilia cordata*, *Pinus nigra* and *Aesculus hippocastanum*, in experimental sites localized in Cluj – Napoca, 2014 - 2015

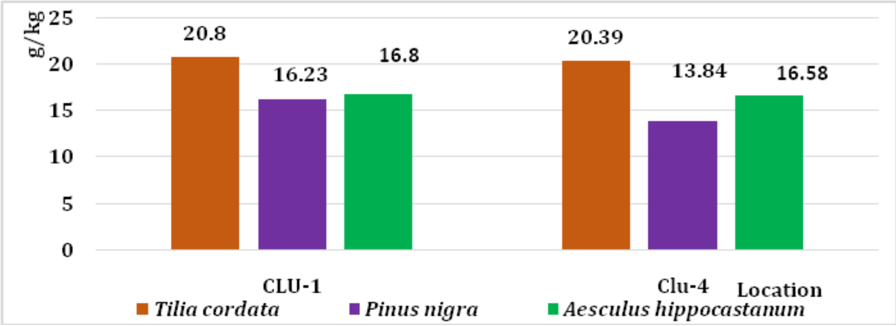

Fig. 3. The evolution of nitrogen concentrations, in foliar tissue of *Tilia cordata*, *Pinus nigra* and *Aesculus hippocastanum* in experimental sites localized in Cluj – Napoca, 2014 – 2015

CONCLUSIONS

The SO_2 evolution, during the experimental period April-September, 2014 and 2015, in the experimental area locate in the proximity of type traffic monitoring station CLU-1, were recorded the highest SO_2 concentration values SO_2 (8.2 µg/m^3), while the minimum values were located in the experimental area located in the proximity of type industrial monitoring station, respectively 7.76 µg/m^3. In the meantime, the NOx recorded the highest concentration (75.5 µg/m^3), while the minimum values were recorded in the experimental area located in the proximity monitoring station of industrial type (CLU-4), 42.4 µg/m^3 NOx, respectively.

Tilia cordata has the biggest capacity of sulphur and nitrogen bioaccumulation, while in *Pinus nigra*, and *Aesculus hippocastanum* have the lowest capacities of sulphur and nitrogen bioaccumulation.

According to the present study, it is recommended planting chestnut species (*Aesculus hippocastanum*) and linden (*Tilia cordata*) in urban areas where there is a risk of sulphur and nitrogen pollution due to their high monitoring capacity of air pollution with the majority of this type of pollutants.

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