*Impact of the Atmospheric Contamination on the Content of Heavy Metals of Water Leaf (*Talinum triangulare*) Harvested in Urban and Peri-urban Farmlands*

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Impacto de la contaminación atmosférica sobre el contenido de metales pesados de Talinum triangulare *cosechada en huertos urbanos y peri-urbanos*

Impacte de la contaminació atmosfèrica sobre el contingut de metalls pesants de Talinum triangulare *collida en horts urbans i periurbans*

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RESUMEN

Se determinaron los contenidos de cadmio, cobre, manganeso, níquel y plomo en *Talinum triangulare* (Jacq.) Willd. en diferentes huertos urbanos y peri-urbanos de La Habana, los cuales fueron clasificados de acuerdo con la contaminación cualitativa del aire con el objetivo de evaluar la influencia de la calidad del aire sobre la concentración de estos metales en la planta. Las determinaciones de los metales se realizaron por espectrometría de absorción atómica usando la sonicación con ácido nítrico a 1 mol·L^{-1} durante 1 hora para llevar la muestra a fase acuosa. Los valores obtenidos oscilaron entre 0,1 – 0,13 ppm para el cadmio; 0,89 – 1,39 ppm cobre; 18,25 – 30,41 ppm manganeso; 0,73 – 1,49 ppm níquel y 0,52 – 0,70 ppm para el plomo. El Análisis de Componentes Principales (ACP) de los resultados mostró que el agrupamiento de las muestras según sus contenidos de metales pesados siguió un patrón similar al de la clasificación de los huertos según la polución del aire, utilizada como criterio para realizar el estudio y por lo tanto el ACP puede ser considerado un estimador de la contaminación atmosférica de los cultivos por metales pesados para trabajos futuros.

Palabras claves: **Contaminación atmosférica. Metales pesados. *Talinum triangulare.***

SUMMARY

The contents of cadmium, copper, manganese, nickel and lead were determined in water leaf (*Talinum triangulare* (Jacq.) Willd.) in different urban and peri-urban farmlands from Havana, which were previously classified according to the qualitative contamination of the air with the objective to evaluate the influence of air quality on the concentration of these metals in the plant. Determinations of these metals were made by atomic absorption spectrometry using sonication with 1 mol·L^{-1} nitric acid during 1 hour to take the sample to aqueous phase. Values obtained ranged from 0,1 to 0,13 ppm for cadmium; 0,89 – 1,39 ppm for copper; 18,25 – 30,41 ppm for manganese; 0,73 – 1,49 ppm for nickel and 0,52 – 0,7 ppm for lead. The Principal Component Analysis (PCA) of the results showed that the grouping of samples according to their heavy metals content followed a pattern similar to that of the classification of farmlands as to air pollution, used as criterion to conduct the study and thus PCA can be considered as an estimator of the atmospheric contamination by heavy metals of crops for further works.

Key words: **Atmospheric pollution. Heavy metals. *Talinum triangulare.***

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RESUM

Es determinen els continguts de cadmi, coure, manganès, níquel i plom en *Talinum triangulare* (Jacq.) Willd. en diferents horts urbans i periurbans de l'Havana, que hom classifica d'acord amb la contaminació qualitativa de l'aire, amb l'objectiu d'avaluar la influència de la qualitat de l'aire sobre la concentració d'aquests metalls en la planta. Les determinacions dels metalls es realitzen mitjançant espectrometria d'absorció atòmica emprant sonicació amb àcid nítric (1 mol.L-1) durant 1 hora per passar la mostra a fase aquosa. El valors obtinguts oscil·len entre 0,1 i 0,13 ppm per al cadmi; 0,89 – 1,39 ppm per al coure; 18,25 – 30,41 ppm per al manganès; 0,73 – 1,49 ppm per al níquel, i 0,52 – 0,70 ppm per al plom. L'Anàlisi de Components Principals (ACP) dels resultats mostra que l'agrupament de les mostres segons els seus continguts de metalls pesants segueix un patró similar al de la classificació dels horts segons la contaminació de l'aire utilitzada com a criteri per realitzar l'estudi, i per tant el ACP es pot considerar un estimador de la contaminació atmosfèrica dels cultius per metalls pesants per a treballs futurs.

Mots clau: **Contaminació atmosfèrica. Metalls pesants. *Talinum triangulare.***

INTRODUCTION

It is well known that the environmental pollution associated to the increase of industrialization and urbanization threatens production, quality and security of foods, which constitutes a danger for human health.

The presence of metallic elements in foods widely varies depending on technological practices of production and manufacture, as well as the degree of environmental contamination (Buchaver and Haghiri, 1973).

Heavy metals are of considerable environmental concern due to their toxicity and cumulative capacity (Omgbu and Kokogbo, 1993; Birley and Lock, 2000). Some metals like cadmium, mercury, lead, nickel and bismuth are considered highly toxic for human health (Zeeuw and Lock, 2000).

Metallic pollutants can be accumulated in crops and some species have more bioaccumulation capacity than others as it is the case of leafy vegetables (Buchaver, 1973), in which the absorption of metals from the contaminated irrigating water, the earth through the roots or the air due to the deposition on the foliage of airborne particles and its subsequent absorption and translocation to different parts of the plants take place (Zeeuw and Lock, 2000). Contamination of leafy vegetables by heavy metals present in the atmosphere is influenced by the characteristics of the species, such as type of tissues of the leaves, their orientation, as well as their form and size that determine a greater or smaller area of deposition. On the other hand, particle size, wind direction and environmental humidity are also factors that influence deposition, retention and absorption of the atmospheric metallic contaminants in the plant (Mulgrew and Williams, 2000).

Urban and peri-urban agriculture constitutes an important food source for the populations of many developing countries. The urban farmlands of the most important cities of Cuba also have the characteristic of being organic, thus they are called "organoponics" by the population. Here, a variety of vegetables are biologically cultivated (with no use of agrochemicals), among which water leaf (*Talinum triangulare*), a leafy vegetable of African origin until now little -known has extended in the last years.

A variety of works (Pilegaard and Johnsen, 1984; Aremu and Udoessien, 1990; Srikanth and Raja, 1991; Adeniyi, 1996; Puschenreiter, 1999; Ni *et al.,* 2002; Yusuf *et al.,* 2003; Finster *et al.,* 2004) reflects the impact environmental contamination by heavy metals is having on urban agriculture, that is why the objective of this work was to evaluate the contents of Cd, Cu, Mn, Ni and Pb in water leaf cultivated in urban and peri-urban farmlands of Havana located in zones of different degree of atmospheric pollution.

MATERIALS AND METHODS

Sampling

To carry out sampling, several urban and peri-urban farmlands of Havana city were classified into four zones of atmospheric contamination by the Department of Environmental Health from the Cuban Ministry of Health: high atmospheric contamination zone (H), medium zone (M), low zone (L) and clean zone (C), according to the quality of the air in which they were located.

Three farmlands per each of these zones of air contamination were sampled for a total of 12 farmlands: 9 urban farmlands (zones of high, medium and low contamination) and 3 peri-urban farmlands (clean zone), during the months of November and December of 2004. The most important considerations taken into account for this classification were: physical-chemical characteristics of different types of pollutants, kind of generating sources, proximity of a group of static important sources of contaminants of the air as it is the case of relevant industries and the proximity of some routes of high automotive traffic by light or heavy vehicles (movable sources of air contamination). The direction and frequency of predominant winds and the visual apparent opacity of air of Ringelmann´s Smoke Chart were also considered.

For sampling, current standard for determinating pesticide wastes in agricultural products (NRAG 165: 1979) of Vegetal Health from the Ministry of Agriculture was used. In each farmland, a general sample was randomly taken from the stonecutters (recommended for less than 5 hectares of crops) avoiding to take from the edges, for a size of representative sample of around 1.5-2 kg of the edible part of the vegetable.

Determination of heavy metals

The samples were dried in stove at 100 °C during 24 hours (Zurera, *et al.,* 1987) and later ground in a mill Planetarium Retsech 60 model PM 4 at 60 rpm until the dust obtained completely passed through a 60-mesh sieve.

For the determination of metals Cd, Cu, Mn, Ni and Pb, an absorption atomic spectrometer Philips PU 1900 was used working with 65 Pa air pressure, a 22 L/min acetylene flow and wavelengths 228.8; 324.8; 279.5; 232 and 217nm respectively. The treatment used to take the analyte to aqueous phase was the sonication in ultrasound bath Fungilab with 1 mol.L^{-1} of nitric acid during 1 hour at room temperature, determining the five elements to each of the 12 samples. Determinations were made in triplicate, reporting the average value in ppm in wet base.

A variance analysis of simple classification was carried out among samples of the different areas of air contamination for each of the metals. When significant differences were found, means were compared by Duncan test of multiple ranks with a 95% confidence.

To know if there were differences among samples from the 12 farmlands according to their content of heavy metals, Principal Components Analysis (PCA) (Hair *et al.,* 1999) was carried out. To perform the PCA, the starting point was a data matrix **n x p** of **p** = 5 variables (metallic contaminants) and n = 12 farmlands. A matrix R was obtained from an autoscaling up one Z; every element $\mathbf{Z_{ij}}$ ($1 \geq \mathbf{i} \geq \mathbf{n}$; $1 \geq \mathbf{j} \geq \mathbf{p}$) was calculated by standardization of the corresponding element **dij** of the original data matrix **D**, $\mathbf{Z_{ij}} = (\mathbf{d_{ij}} - \bar{\mathbf{d}}_{\mathbf{j}}) / \mathbf{S_j}$, where $\mathbf{d_j}$ is the arithmetical mean and **Sj** is the standard deviation of **n** elements of the vector **j**. The matrix **R** was used as initial matrix in the analysis of main components. For that purpose, the program Statistica 6.0 (StatSoft, Tulsa) was used.

RESULTS AND DISCUSSION

Table I shows concentrations of the metallic elements of water leaf from different farmlands and average concentrations and standard deviation of them per each zone of air contamination. From the analysis of variance for every heavy metal, no significant differences among different zones were obtained, except in copper, in which the zone of medium contamination was significantly different from the rest.

The multi-variable statistical analysis allows obtaining the distribution and interpretation of many variables of a system as a whole. This approach is important, particularly in data where generally, it is not possible to find differences when they are analyzed separately. Its use here allows, through determining the concentration of a group of metallic contaminants (variables) in the water leaf, the differentiation of samples coming from the organic farmlands located in zones with different degrees of air contamination, taking into account its possible relation with the heavy metal content of the vegetable.

The results of Principal Component Analysis (PCA) appear in Figure 1, where three groups of samples can be obser-

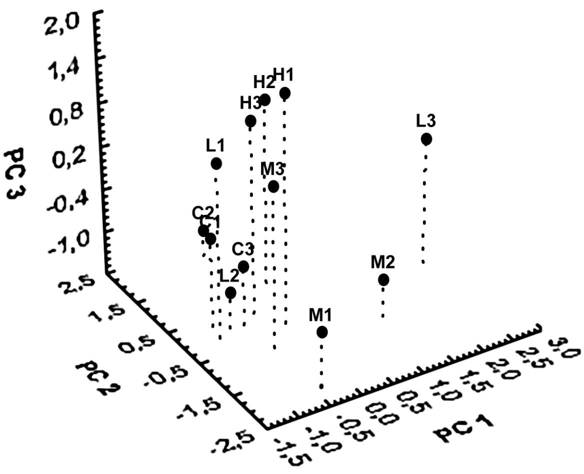

Figure 1. Three dimensional plots of score from PCA.

Legend:

$H_{1,2,3}$: Samples corresponding to three organic farmlands with high air pollution

$M_{1,2,3}$: Samples corresponding to three organic farmlands with medium air pollution

$L_{1,2,3}$: Samples corresponding to three organic farmlands with low air pollution

$C_{1,2,3}$: Samples corresponding to three organic farmlands with no air pollution

TABLE I

Heavy metals concentrations (ppm) in wet base (92% wet) of water leaf from urban and peri-urban organic farmlands with different air pollution.

Metal	Zone H	Zone M	Zone L	Zone C
Cadmium	0.14 0.12 0.13 **0.13 (0.01)**	0.08 0.12 0.11 **0.10 (0.02)**	0.09 0.09 0.20 **0.13 (0.07)**	0.09 0.11 0.11 **0.10 (0.01)**
Copper	1.23 0.92 0.93 **1.03 (0.18)**	1.42 1.36 1.38 **1.39 (0.03)**	1.16 0.87 1.22 **1.08 (0.19)**	0.92 0.71 1.02 **0.89 (0.16)**
Manganese	17.79 29.10 7.86 **18(11)**	10.51 42.09 24.36 **26 (16)**	19.95 13.93 45.62 **27 (17)**	16.34 52.81 22.09 **30 (20)**
Nickel	1.26 1.82 1.39 **1.49 (0.29)**	1.06 1.70 0.79 **1.18 (0.47)**	0.85 0.87 2.17 **1.30 (0.76)**	0.81 0.76 0.63 **0.73 (0.09)**
Lead	0.73 0.70 0.66 **0.70 (0.04)**	0.45 0.40 0.70 **0.52 (0.16)**	0.77 0.49 0.42 **0.56 (0.19)**	0.61 0.61 0.54 **0.59 (0.04)**
Average values and (standard deviations) appear in bold.				

ved: One involving the samples of the organic farmlands C_1, C_2, C_3 and L_2, differentiated by the first principal component; another with the samples H_1, H_2, H_3, L_1 and M_3, differentiated by the second main component and a third corresponding to the rest of the evaluated samples M_1, M_2 and L_3.

Thus, the grouping of samples coming from the organic farmlands approximately reproduced the zones of different air contamination where they were located. Nevertheless, there is overlapping in this case since only three groups of samples were differentiated while the classification of farmlands was made in four zones of air contamination. It can be observed in the same figure, that while the samples of organic farmlands of extreme zones, that is, clean and high zones, are well differentiated and they are in two different groups, those corresponding to farmlands with low and medium contamination were inserted in some of these three groups but following a logical sequence in which, for example, one sample coming from a farmland with low pollution air (L_3) is overlapped with two samples from medium air pollution and another sample of low pollution zone (L_2) overlapped with the three samples of the clean zone group. The only exception in this distribution of the 12 samples studied was L_1 which fell into the group in which the samples corresponding to high air contamination are.

Paying attention to factors loading (Table II) of each of the main components, Cd and Ni metals contribute more for PC 1; Cu significantly contributes for PC 2, while for PC 3, only Pb contributed. Manganese, being the metal that is in a concentration much greater than the rest of metals (Figure 2) did not contribute to any of the components or its contribution in this distribution was not important, probably because its accumulation as contaminant in the plants is more related to the absorption from the ground than that from the air.

As it can be seen in Table III, the first two main components (PC 1 and PC 2) are those of greater explanation of the system variance (67.96 %), whereas PC 3 explains the 17.32 %, for a total of 85.28 % of explanation of total variance, which is a good value given the heterogeneity of heavy metal concentrations of samples from different organic farmlands (Table I).

TABLE II

Loading of the variables on the PCA.

Variable	PC 1	PC 2	PC 3
Cadmium	0.8583*	0.1753	0.3459
Copper	0.2797	0.8740*	0.1615
Manganese	0.6588	0.4649	-0.3136
Nickel	0.8663*	-0.0458	0.2905
Lead	0.5282	0.3267	0.7332*
* significant differences at $p < 0.05$			

TABLE III

Eigenvalues and accumulative percent of total variance derived from PCA.

PC	Eigenvalues	Total Variance (%)	Cumulative Variance (%)
1	2.2784	45.57	45.57
2	1.1196	22.39	67.96
3	0.8658	17.32	**85.28**

These results of the PCA allowed to know and infer that there is a relationship between the atmospheric contamination as a whole (qualitative criterion) and the heavy metal concentration in the air and, at the same time, this is also related to the heavy metal concentration of water leaf, that is, although it was impossible to make direct measurements of the concentration of these metals in the air (quantitative criterion), which is difficult and expensive and equipment was not available, the qualitative criterion used for the classification of the air in zones of high, medium, low and clean, can be considered an estimator of the atmospheric contamination by heavy metals of edible plants for future works.

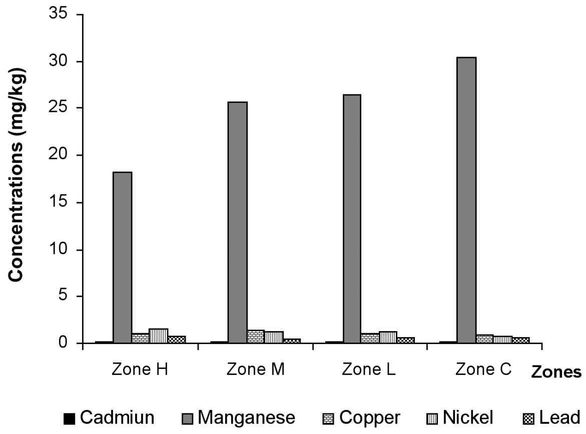

Figure 2. Average concentrations of metals Cd, Cu, Mn, Ni y Pb (mg/kg) in water leaf from urban and peri-urban farmlands with different air pollution.

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