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Preliminary research concerning the distribution of copper in the soil and vegetables in historical anthropic pollution (Caras-Severin County, Romania)

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Abstract

The authors present data concerning the distribution of copper in the soil and vegetables (carrots and parsley) in two areas of Caras-Severin County (Ruschiţa and Moldova Nouă) known as historical anthropic pollution areas, and in two unpolluted areas (Borlova and Golet), considered reference (control) areas. Results of soil, carrot, and parsley sample analysis in the areas with historical anthropic pollution show high concentrations of copper both in the soil and vegetables, in some cases possibly toxic, compared to the concentrations of the two control areas (Borlova and Goleţ).

Keywords: copper, soil, carrots, parsley, contamination

1. Introduction

Vegetables and fruits have important role in the development of the human body. Food and therapeutic quality of carrot and parsley is given by the nature and quantity of nutrients contained in them [1,3]. Copper is an important micro-bio-element contained in carrot and parsley, with essential roles in the effective exercise of the human body: it has important role in the production of enzymes that protects against certain toxic substances (free radicals, cadmium), intervenes in the formation of the connective tissues that serve to develop a variety of other tissues participates in energy production contributes to the absorption of iron, preventing anemia: is involved in producing neuro-chemical substances essential to the proper functioning of the brain, nerves and muscles functions; influences the immune system, reduces the production of histamine, which reduces allergic manifestations, etc. [2].

Carrot is a precious vegetable for human nutrition, due to its rich content in vitamins A, B, C, carotene, sugars, dextrose, mineral salts, iron, phosphorus, calcium, sodium, potassium, magnesium, arsenic, manganese, sulfur, copper, bromine and asparagines.Parsley is one of the most famous and popular vegetable, the root and its leaves are used both raw and processed in various dishes. Due to its composition: rich in vitamin C, B and E, provitamin A, iron, manganese, calcium, phosphorus, magnesium, potassium, sulfur, iodine, chlorophyll, and an amino acid called histidine, parsley is a general tonic, an antioxidant that is purifying the body, strengthens immunity.

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Above certain concentration limits, copper and trace elements essential for the body can become toxic. Maximum permissible concentration of copper carrot and parsley root is 5 mg / kg [6]. Therefore, the food products with role in the development of the human body should be assessed both as a source of energetic, plastics and stimulatory nutrients and as a source of vehicular pollutants to impact more or less serious physiological functions vital to the body [3].

The results obtained from analysis of soil samples, carrots and parsley in areas with anthropogenic pollution shows higher copper concentrations both in soil and in vegetables.

2. Materials and Methods

*Reagents and solutions.*The stock standard solutions (1000 mg/L) were analytical grade purchased from Riedel de Haen (Germany). The working solutions were prepared by diluting the stock solutions to appropriate volumes. The hydrochloric acid 32%, nitric acid 65% and H_2O_2 25% solutions used were of ultra pure grade, purchased from Merck (Germany). All reagents were of analytical-reagent grade and all solutions were prepared using deionized water.

*Soil samples preparation.*Soil samples were sampled with agrochemical steel probe, from 0-20 cm deep, within the cultivated area. In laboratory the soil samples were dried in clean air, ground and passed through a 2mm sieve to remove roots, stones and other large particles. The soils were analyzed for total contents of copper contents after digestion in *aqua regia.* 10mL mixture of nitric acid and hydrochloric acid (3:1) was added to 5.0 g of soil samples and heated on a hot plate. Then, residue were treated with 1N nitric acid, centrifuged and finally adds to 25 mL in quoted flask. For the determination, the standard working solutions were prepared with the same extraction solution.

*Carrots and parsley samples preparation.*Copper content in vegetable samples were analyzed after wet digestion with mineral acid. After washing with deionized water the vegetables were homogenized by mincing. After homogenization, 100 g materials were transfered in quartz capsule, dried at 105^0 C and after cooling the samples were homogenized by mincing. 1g of each dry sample was submitted digestion with 10 mL pure HNO_3 and 10 mL H_2O_2 at 170 ^{0}C in a digest device Digestion System 6-1007 Digester, provided by Tecator. After the complete digestion of the sample solutions were filtered, made up to 50 mL with deionized water. This solution was used for Cu analyze by FASS in air/acetylene flame using an aqueous standard calibration curve. All analyses were made in triplicate and the mean values were presented.

*Sample analysis.*Atomic absorption spectrometry in air-acetylene flame presents a sufficient sensibility for the direct determination in the acid solution resulted after digestion. Analysis of Cu was made with ContrAA-300, Analytik-Jena device, by flame atomic absorption spectrometry (FASS) in air/acetylene flame.

*Statistical analysis.*The data were statistically analyzed using a statistical package MVSP 3.1.

3. Results and discussions

The copper content of the studied samples is presented in figure 1. The distribution of copper in the soil and vegetables in historical anthropic pollution areas were studied using FAAS method and statistical analysis program MVSP 3.1. In tables 1 and 2 are presented the romanian standard values for copper in soil and studied vegetables as well as the warning and intervention tresholds. According to this data, in soil samples from Ruschita the content of copper is higher than the warning treshold (100 mg/kg dry mater) and in Moldova Noua the content exceeds the intervention treshold (200 mg/kg dry mater). Also the parsley root samples from Ruschita and Moldova Noua present dangerous accumulation of copper (figure 1). It seems that parsley root is accumulating more copper then carrot roots.

Table 1. Excerpt from Romanian Agriculture Ministry Ordinance 756/1997, standard values for copper in soil [5]

Experimental values [mg/kg dry mater]	**Cu**
Normal values	20
Warning threshold	100
Intervention threshold	200

Table 2. Excerpt from ministry of public health ordinance no 975/1998 , maximum limits accepted for copper in food [6]

Food	**Cu (mg/kg fresh product, ppm)**
Fresh or deep - frozen vegetables except for leaf vegetables	5.0
Fresh or deep – frozen fruits	5.0

Correspondence Analysis CA allows an assessment of copper content data corresponding to the samples of soil, parsley and carrots, using the square root of their transposed matrix (figure 2).

Parsley roots are accumulating more copper than carrot roots, observation that is confirmed by correspondence analysis (figure 2) as well as principal component analysis (figure 3).

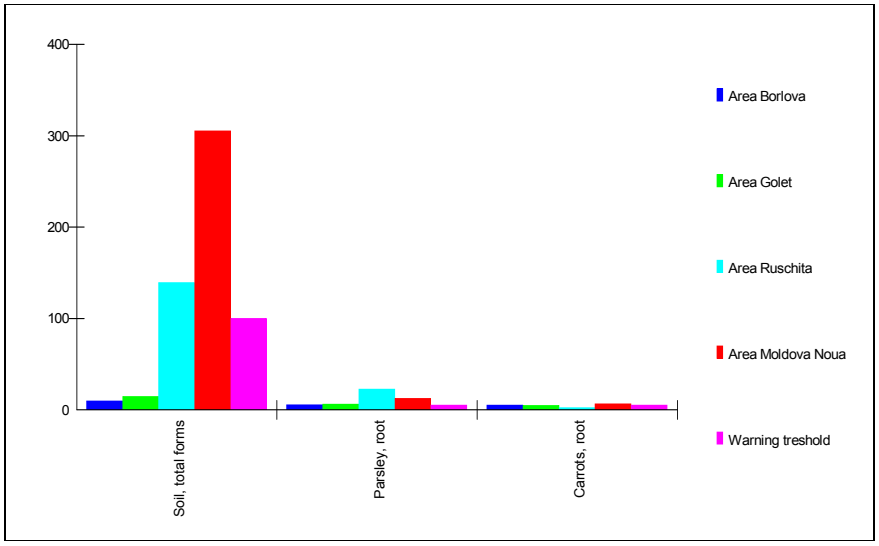

Figure 1. FAAS copper content

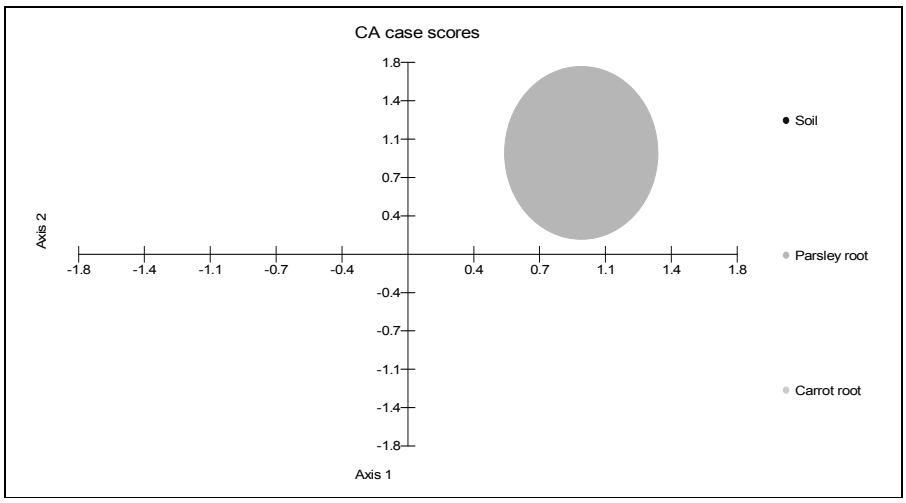

Figure 2. CA case score bubble representation of copper content

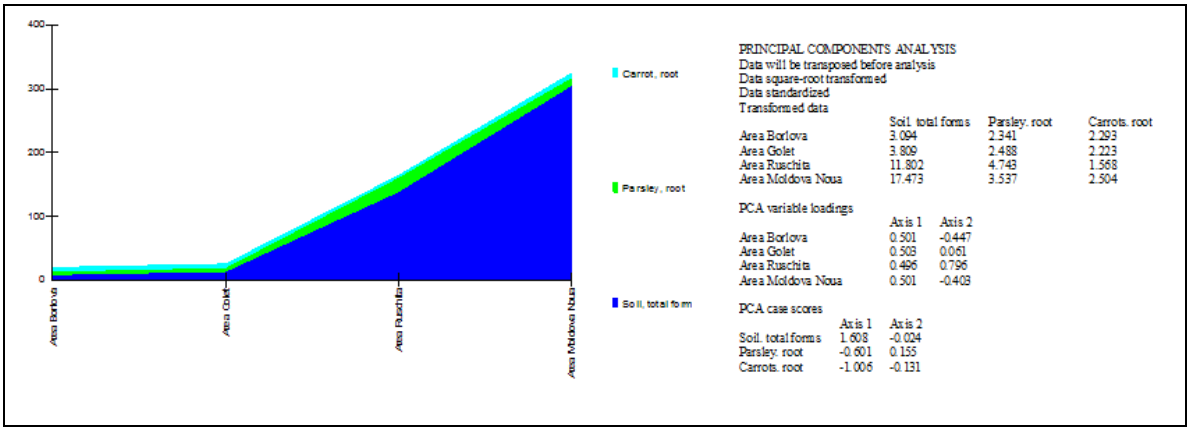

Figure 3. PCA graphical representation of copper content distribution in the studied samples

4. Conclusion

1. Heavy metals need to be monitorised and people need to be informed regarding the values registrated at soil and vegetables levels in order to prevent cultivation of vegetables that are accumulationg high concentration of that specific element that could endanger the health of the consumers;
2. Copper is accumulated especially in parsley roots, so in the area where the soil is having a high concentration of copper, parsley should be avoided to be cultivated;
3. In accordance to literature studies, metal absorption and accumulation in plant depend on a few soil factors, such as: pH, clay content, organic matter content, cationic exchange capacity, nutrient balance [4];
4. Hence, copper accumulation should be studied more thoroughly in plants those roots are consumed.

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