

ASPECTS OF TRANSFER HEAVY METALS IN RASPBERRY (*RUBUS IDAEUS*) GROWN IN THE GEOGRAPHIC AREA OF NĂDRAG (CARAŞ-SEVERIN)

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ABSTRACT

Ensuring of raspberry for human consumer (spontaneous and/or cultivated flora), harvested within Timis and Caras Severin mountain area (Nădrag), is the important segment for food processors work in this area. Raspberry as fruit or as a flavoring, juice, etc.. is obtained from the fruits by processing, prior centrifugation and a short fermentation. Through all these steps it can be naturally contaminated, by mass transfer, with heavy metal cations by leaching, complexation, or selective salification. Researched areal is located in a mountainous area, coldish, wet, whit soil characteristics that can facilitate the transfer and/or accumulation of heavy metal cations (mobile forms and/or total forms) up to the limit of tolerance (*Cu, Pb, Zn, Co, Fe*, etc.).

Keywords: *heavy metals, raspberries, cationic transfer, contaminants*

INTRODUCTION

From the climate data colleted can observe the are not significant differences between year and multi-year averages for temperature (*9-10,5°C*), relative humidity (*86-93%*), volume of rainfall (*800 – 900 mm/year*) and for sunshine duration (*1784 ore/year*). During the study, These data can be considered reference of this area, creating normal conditions to uptake of heavy metals in this plants grown in this area [1].

Nădrag village area is characterized by a rugged terrain and different types of soils, lithosols, rendzina, Regosol and Cambiosol. They are characterized by massive skeleton (parental rock), pH values vary from acid to alkaline, variable contents of humus and generally low and very low amount of phosphorus and low amount of potassium.

From these data we can see that the soil, on which raspberry crops were located, is a typical rendzina on limestone with a alkaline reaction, with fine textured (clay/clay lute), medium-high humus content, low content of phosphorus and mobile potassium.

References found records that the area has increased content of heavy metals, data found after experimental work and chemical analysis of soil (The concentration of heavy metals - total forms of soil this area).

MATERIALS AND METHODS

Materials

1. Raspberries fruits (*Rubus Idaeus*) from 2010's fruit harvest in Nădrag area (Caraş Severin county).
2. All reagents (selective list) were analytical grade (Sigma Aldrich) and specific for atomic absorption spectral analysis.

Methods

Following analytical sequence was taken:

- pre-concentration of heavy metals acid extracts, when the concentration was below the analytical detection limit;
- comparison of experimental results obtained with the same analytical method in different laboratories or with different methods in order to establish their accuracy;
- comparison of experimental results obtained in the investigated areas and with those from the literature.
- multivariate analysis (PCA - principal component analysis) to experimental data.

RESULTS AND DISCUSSION

The concentration of heavy metals - total forms of this area soil.

It is an uniform distribution of heavy metals in soil (0-40 cm), confirm that the concentrations of heavy metals are much lower. This is explained by the fact that in **EDTA** solution - ammonium acetate, at **pH = 7.00**, are extracted exclusively the available amounts of heavy metals for bush, and the existing mobile forms in soil solution. The well represented metals were manganese, iron and zinc, with a concentrations from **11.32 ppm (Zn)** to **51.1 ppm (Fe)**. Other elements are in low content (**Cu** and **Pb**) or very low (**Co**, **Ni**, **Cr** and **Cd**), between 0,34-0.92 ppm.

Comparing experimental values with the limit recommended by the literature for some toxic metals, it appears that, excepted cadmium content, which is very close to the limit, the other values are below of the levels toxicity. Special mention is required for cadmium, which in some soil samples was found in higher concentrations than the limit, although the mean values are below to the limit of toxicity.

Noted, however, increased concentrations for **Mn**, **Cd**, **Cr** and **Pb**, close to the interference limit or over intervention limit values [2].

The experimental results obtained from analysis of soil from Nădrag area confirms that it has increased amounts of heavy metals - total form, above the normal limits, sometimes near to the alert limit (especially for manganese and lead) or near intervention limits (in the case of cadmium).

As the mobile forms of heavy metals in soil are, generally, responsible for the amount of metals that can be gained in raspberries, this were determined in **EDTA** extract - ammonium acetate [3]. The obtained values are similar.

Analyzing the experimental results concerning the main physico-chemical characteristics in soil, it can be concluded that soil from studied area it fall into the category of geogen soils loaded with heavy metals, especially zinc, manganese, cadmium and lead. Some physico-chemical properties of this soil type (high capacity of retention for heavy metals, weakly alkaline reaction, relatively high content of humus, etc.) reduces substantially the transfer of mobile forms, accessible in raspberries. This explains the values content of heavy metals in mobile forms, which fall generally, within the normal range of this area.

Due to its physico-chemical properties (composition, pH, etc.) **water** can be one of the factors that can influence the accumulation of heavy metals in raspberries. The concentration of heavy metals in surface water from the raspberry crop is within the tolerances limits presented in literature. Reaction of water from land surface is low alkaline, pH average is **pH = 7.8** [4].

From the experimental results obtained in determination of heavy metals, we find that concentrations of heavy metals in raspberry is within the normal range for this type of fruit. Slightly higher values, compared with values obtained near this area, is due to intense mineralizations of Nădrag area. Heavy metal distribution is uniform, the average concentrations ranging from **0.12 ppm for cadmium** to **9.20 ppm for iron**.

Iron, essential bioelement in body, his concentration was higher than the rest of the analyzed elements.

Manganese, zinc, copper and **lead**, compared with iron, were determined in much lower concentrations and very close to each other, from **0,45 ppm** to **0.69 ppm**.

Cobalt and **nickel** were found in smaller concentrations, average composition is only **0.21 ppm** and respectively **0.10 ppm**.

Cadmium, metal with the most pronounced toxic characteristics, was detected in the lower amount (whit an average of **0.012 ppm**).

Comparing the experimental average value whit maximum limits admitted for toxic metals or potentially toxics: **Cd, Pb, Cu** and **Zn**, we find that the allowed level of toxicity not exceeded for this type of plant food [5].

It should be noted that, however the average value for content of heavy metals are below the limits of toxicity, are recorded and isolated cases, "accidental", where the concentration of some metals (**Pb** and **Cd** in small extent) is near or over the maximum allowed level [6].

It can be concluded that the heavy metals concentrations in the raspberry, grown in this area, generally is situated within the normal limits for this type of fruit. Increased values, in comparison with adjacent areas considered unpolluted, are attributed to the increased content of heavy metals in soil. Under these conditions, the translocation mechanism of metals in soil, specifically for raspberry bushes does not allow storage of some heavy metal quantities, above allowed toxicity limits.

Regarding the distribution of heavy metals between: Grass – Leaves – Raspberry, is found a decrease of concentrations in iron, manganese, zinc and cadmium. Content differences between leaves and fruits are small or insignificant for copper, nickel and cobalt.

CONCLUSIONS

✓ Climatic parameters, of the Nădrag village area, creates normal condition for assimilation of heavy metals.

✓ The soil is characterized by a high content of heavy metals - total forms, above the normal limits, sometimes at the alert level (especially for **manganese** and **lead**) or intervention level (for **cadmium**).

✓ Analyzing the experimental results, concerning to main physico-chemical soil characteristics, it can be concluded that studied soil fall into the category of loaded soils with heavy metals, especially **zinc, manganese, cadmium** and **lead**.

✓ Physico-chemical properties of the soil: higher retention capacity of heavy metals, weak alkaline reaction, relatively high humus content, etc., reduces substantially the transfer of heavy metals in mobile forms.

✓ Concentration of heavy metals in mobile forms, fall generally, within the normal limits for this area.

✓ Experimental values obtained from analysis of heavy metals in raspberry, harvested in this area, is generally within the normal range for this kind of fruit, below the levels of toxicity. Increased concentration values of heavy metals, in comparison with adjacent areas, is due to additional load of soil with such metals.

✓ Under these conditions, the mechanism of translocation of metals from soil to fruit, does not allow storage of high quantities of heavy metals in raspberry. Therefore, in the investigated area are not obvious points of pollution / contamination of fruit with heavy metals.

✓ Distribution of heavy metals in soil - grass vegetation – raspberry leaves - raspberry, as in the surrounding areas, depends mainly on the concentration of heavy metals

in soil solution (mobile forms). The highest levels have been identified in herbaceous vegetation, especially the best represented heavy metals (*iron*, *manganese* and *zinc*), *cadmium*, *copper* and *nickel*. In the case of *cobalt* and *lead*, there are content differences between: herbaceous vegetation - leaves – fruits, but are insignificant.

✓ Regarding the distribution of heavy metals between: grass - leaves - fruits, there is a decrease of concentrations for *iron*, *manganese*, *zinc* and *cadmium*. The differences content between leaves and fruits are small or insignificant for copper, nickel and cobalt.

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