ORIGINAL PAPER

DETERMINATION OF Cu AND Zn IN SAMPLES OF GRAPE AND SOIL FROM MURFATLAR VINEYARD

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Abstract. *Grapes and grape products are important sources of fiber, nutrients and minerals to the human body. For example, zinc and copper are two elements that are found in all parts of grapes (seeds, pulp, skins). In optimal concentrations, they are beneficial. If, however, it exceeds the daily dose of zinc (overdose), can occur several adverse reactions in the stomach (heartburn, nausea), tiredness, weakness. Copper overdose can lead to poor absorption of other essential minerals for the body (iron, calcium, magnesium, etc.). The aim of this study is to analyze the level of Zn and Cu in* Vitis Vinifera L. *grapes fruits and soil from the Murfatlar city, Constanta, Romania. These elements were quantified by flame atomic absorption spectrometry (FAAS) after the chemical mineralization of the samples with nitric acid and hydrogen peroxide in a Digesdahl device. It can be noticed that the values of cooper and zinc concentrations from both kind of samples (grapes and soil) were lower than the recommendable maximum limit of these metals in fruits respectively soil.*

Keywords: *Cu, Zn, Grape, Soil, FAAS.*

1. INTRODUCTION

A balanced diet involves daily consumption of fruits and vegetables that provide an optimal intake of minerals such as Ca, Mg, Zn, Fe, Cu, Se, elements necessary for the proper functioning of the body. In optimal concentrations, they are beneficial: zinc helps to boost immunity, fight colds, reducing macular degeneration, wound healing or ADHD; copper is anti-infective, anti-inflammatory, anti-tumor. Copper and zinc facilitate the functioning of many metabolic enzymes [1].

Copper and zinc are essential trace elements in plants and animals. Excessive absorption of zinc suppresses copper and iron absorption. The free zinc ion in solution is highly toxic to plants, invertebrates, and even vertebrate fish [2, 3].

Soil is a complex mixture, heterogeneous both organic and inorganic compounds in solid as well as liquid solution. Plants found here all the substances necessary to multiply and

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grow. Soil composition influence plant metabolism and concentration of various minerals in them [4].

Generally, heavy metals are present in the soil at low levels, but, because of anthropogenic causes (industry, agriculture, municipal waste materials) or occurrence of geochemical anomalies it is possible to measure high contents of risk elements (Pb, Cd, Cu, Zn, Hg). The presence of metal concentration in the plants depends on the presence of the metallic elements in water as well as in soil [5].

The aim of this work was to determine Cu and Zn in peel, seed and pulp of five grapes samples from Murfatlar vineyard. Also it was to determine those metals in the soil samples collected from the same grape varieties at different depths: surface, 20 cm and 40 cm.

2. MATERIALS AND METHODS

2.1. MATERIALS

Analytical grade chemicals (HNO_3>69%, hydrogen peroxide 30%, Cu^{2+} and Zn^{2+} certified analytical standard solutions of 1000 mg/L purchased from Merck and Fluka) were used. All chemicals were of analytical reagent grade (purity > 98%) and used without further purification. All the solutions were prepared using ultrapure water from a Milli-Q Elix3 system.

Five varieties of Murfatlar grapes were studied: Cabernet Sauvignon, Riesling Italian, Pinot Noir, Columna and Mamaia. Samples were taken during ripening grapes in the vineyard Murfatlar, in three different times during August 17-September 9, 2013.

A homogeneous sample of each varieties fresh grapes from the Murfatlar vinegard was collected. In order to determine metal concentrations, the samples were washed with deionized water, carefully separated into peel, pulp and seeds, dried and homogenized. 0.5-0.9 grams of each dry sample was subjected to digestion with 8 mL HNO_3 65% and 10 mL H_2O_2 25% at 150^oC in a Digesdhal device provided by Hach Company. After the complete digestion, the samples solution was filtered and transferred to a 50 mL volumetric flask with deionized water.

Soil samples were collected from each of five varieties of selected plant samples origin in at three depths: surface, 20 cm and 40 cm simultaneously. 5g of soil samples from the selected sites were dried at 105 ^0C to constant weight. Then, 10mL distillated water was added, homogenized and dried for one hour at sand bath. The samples were digested with 10mL HNO_3 2% for two hours. The mixtures were filtered and diluted to 50mL deionized water.

Analysis of the filtered mixture was conducted by Atomic Absorption method [6]. Analyses were made in triplicate and the mean values are reported. The FAAS instrument used was a GBC Avanta Flame Atomic Absorption Spectrometer. Concentrations of metals were measured using monoelement hollow cathode lamp.

2.2. METHODS

Cu and Zn were determined by flame atomic absorption spectrometry (FAAS) in air/acetylene flame using an aqueous standard calibration curve (*Figure 1*) with a correlation coefficient of 0.9985 for Zn and 0.9998 for Cu. Acetylene of 99.99% purity at a flow rate of 1.2 L/min was utilized. The main characteristics of the equipment for metals determination are: copper was determined at 324.7nm and zinc at 213.9nm. The curve was linear in the concentration range 0.2-5.0mg/L for Cu and 0.2 si 2.0 mg/L for Zn.

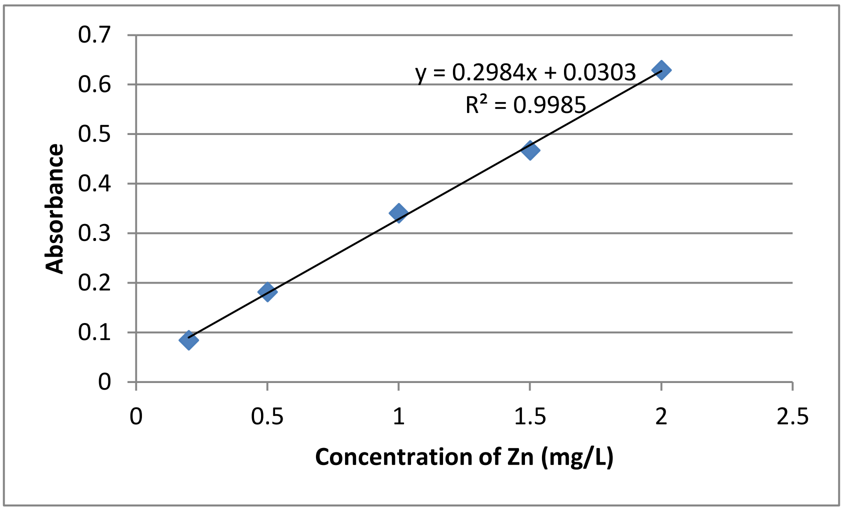

Figure 1. A typical competitive curve for Zn.

3. RESULTS AND DISCUSSION

3.1. RESULTS

Figure 2 presents the average values of Cu and Zn concentrations in peel, pulp and seed of different varieties of grapes. The highest metal concentration found is zinc (3.57 mg/Kg), while cooper was 3.45 mg/kg in fruits seed assessed. The recommendable maximum limits for metals in fruits are 5 mg/Kg for Cu and Zn [7, 8]. It can be noticed that the values of Cu and Zn concentrations in grapes are lower than the recommendable maximum limit of these metals in fruits.

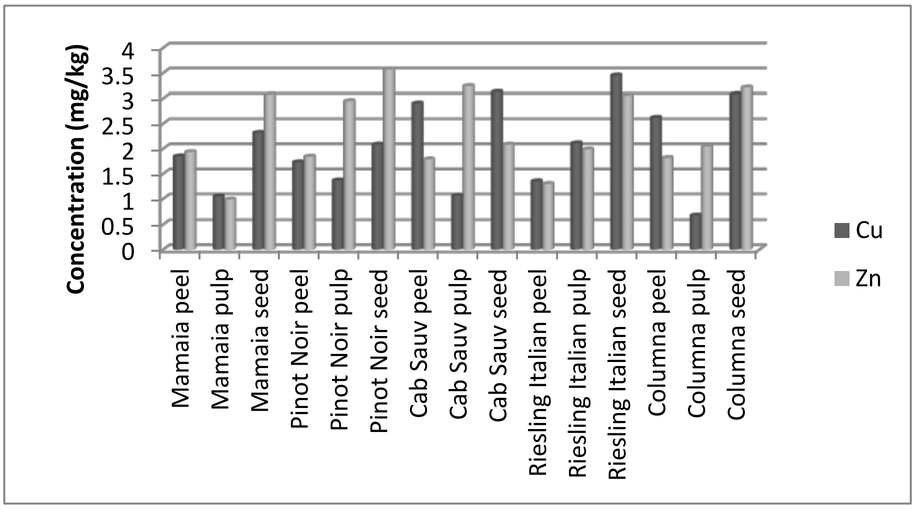

Figure 2. Cu and Zn occurrence in peel, pulp and seed of five varieties of grapes (Cab Sauv – Cabernet Sauvignon).

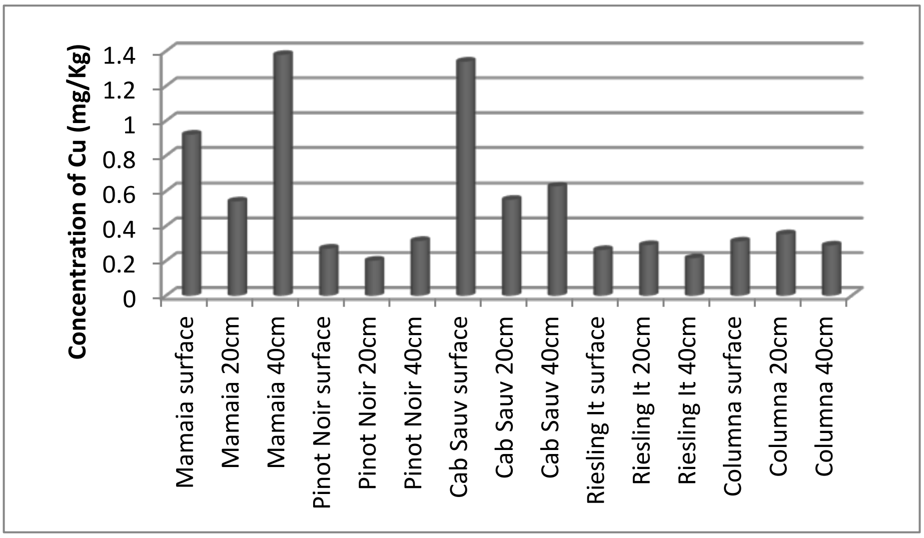

Figure 3. Copper soil levels for five varieties of grapes at three depths.

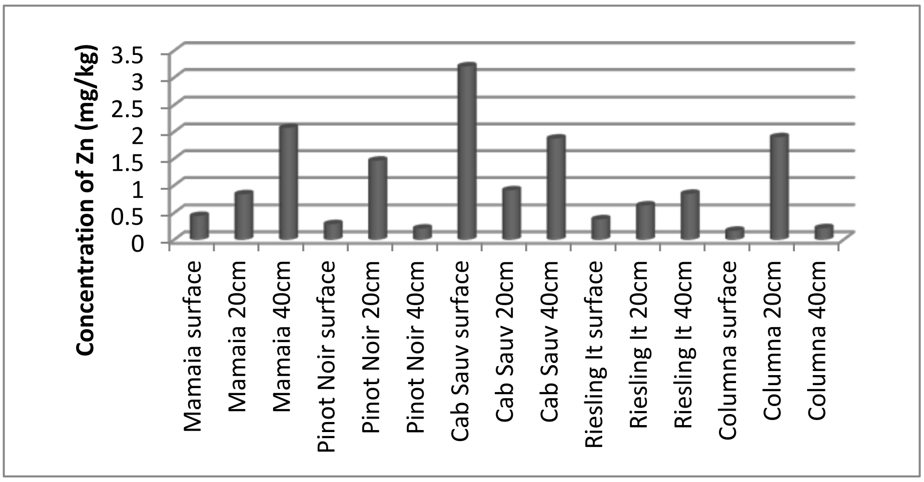

Figure 4. Zinc soil levels for five varieties of grapes at three depths.

3.2. DISCUSSIONS

In literature, the amount of copper varies. For example, Ko et al. found 8.45 mg/kg copper in Cabernet Sauvignon variety and 8.35 mg/kg in Chardonnay variety, in New Zealand vineyards [9], much higher values than those of this article. Angelova et al. found 3.6mg/kg cooper in skins of grapes, 0.3mg/kg cooper in pulp and 7.6mg/kg cooper in seeds of grapes of Pleven region, Bulgaria. Also, they found 4.3mg/kg Zn in skin, 0.2mg/kg in pulp and 7.5mg/kg Zn in seeds of grapes of the same region. These results are higher than our results from the Murfatlar region [10].

Physiologically, zinc accumulates in grapes, in amounts of only 1.5-2.5 mg/L of grape juice. The physiologic contribution is extremely low accumulation of copper in the grapes: 2-7 ppm/L of grape juice. In addition to the physiological intake in minerals, grapes may become contaminated with some exogenous minerals from pesticide residues remained on grapes after phytosanitary treatments (Cu^{2+}, Zn^{2+}, Mg^{2+}) [11].

Total copper content of agricultural soils in our country was found between 4.3 to 49.7 ppm. Depending on the distance from the emission source, zinc reached values exceeding 5-10 times the typical soils of the area unaffected by pollution [12].

Among the analyzed metals, zinc had the highest concentrations up to 3.20 mg/kg in all the sampling soil, while cooper shows the low concentrations up to 1.37 mg/kg.

Evaluation of Cu and Zn in soils of Murfatlar vinegard showed that amounts of zinc and cooper metals in the soils samples were lower than the recommendable maximum limit of these metals in vinegard soils, *figures 3* and *4*. The regular limit of these metals in vinegard soils were 100mg/kg for zinc and 20mg/kg for cooper [12].

Zinc is present in soils, in the amount of 10-30ppm. In Romania's arable soils can be found in concentrations of 10-97ppm [12].

Of all the trace elements, copper forms the most stable bond with organic material that can be linked up to 50% of the total copper. The vineyard soils accumulate up to 400ppm copper, by spraying with Bordeaux mixture. It remains in the top 20 cm of soil and is not harmful to the vine because its reticular system is under 40 cm. Cupric toxicity usually occurs in soils low in organic matter and those with acid and very acid reaction [12].

4. CONCLUSIONS

The original data in this paper shows copper and zinc content of the grapes and soil. Samples were collected from Murtfatlar vineyard County. Constanta, during August-September 2013.

It measured the concentration of copper and zinc in the skin, pulp and seeds of grapes. It can be seen that the accumulation of minerals copper and zinc is in the solid parts of the grapes (seeds, skins) and in the pulp beans less.

In soil samples analyzed, the concentrations of the two metals does not exceed the maximum permissible concentrations by European standards. So Murtfatlar area proves to be an area untouched by pollution and the grapes harvested here can be consumed by the public.

REFERENCES

[1] Cetina, E. S., Altinöz D., Tarcan E., Baydar, N. G., *Industrial Crops and Products,* **34**, 994, 2011.
[2] Sharma, R.K., Agrawal, M., Marshall, F.M., *Environ. Poll.* **154**, 254, 2008.
[3] Oymak., T., Tokalioglu, S., Yılmaz, V., Kartal., S., Aydin, D., *Food Chemistry,* **113**, 1314, 2009.
[4] Waoo, A.A., Khare, S., Ganguli, S., *Journal of Environ. and Human* **1**(2), 2373, 2014.
[5] Diaconu, D., Nastase, V., Nanau, M.M., Nechifor O., Nechifor, E., *Environmental Engineering and Management Journal* **8**(3), 569, 2009.
[6] Lupascu, N., Chirila E., Munteanu, M., *Ovidius University Annals of Chemistry*, **20**(2) 232, (2009).
[7] *** Ordinul nr. 975/1998 al Ministerului Român de Sănătate Publică. Limite maxime admise ale metalelor în alimente
[8] *** COMMISSION REGULATION (EC) No 1881/2006 of 19 December 2006 Setting maximum levels for certain contaminants in foodstuffs.
[9] Ko, B.G., Vogeler, I., Bolan, N. S., Clothier, B., Green, S., Kennedy, J., *Science of the Total Environment* **388**, 35, 2007.
[10] Angelova, V. R., Ivanov, A. S., Braikov, D. M., *Journal of the Science of Food and Agriculture* **79**, 713, 1999.
[11] Ţardea, C., Sarbu, Gh., Ţardea, A., *Tratat de vinificatie,* Editura “Ion Ionescu de la Brad”, 2000, 89
[12] Chirilă, E., *Chimie şi monitorizarea mediului. Note de curs*, Editura Ovidius University Press, 2001, 48.