



## Determination of Cadmium, Copper, Iron, Nickel and Zinc in Turkish Grape Seeds

EKREM TUSAT<sup>1</sup>, MEHMET MUSA ÖZCAN<sup>2,\*</sup>, FATİH ER<sup>1</sup> and FATMA GÖKMEN<sup>3</sup>

<sup>1</sup>Selcuk University, Cumra High Educational College, 42500 Cumra, Konya, Turkey

<sup>2</sup>Department of Food Engineering, Faculty of Agriculture, University of Selcuk, 42031 Konya, Turkey

<sup>3</sup>Department of Soil Science, Faculty of Agricultural, Selcuk University, 42031 Konya, Turkey

\*Corresponding author: Fax: +90 332 2410108; Tel: +90 332 2232933; E-mail: mozcan@selcuk.edu.tr

(Received: 31 December 2010;

Accepted: 27 May 2011)

AJC-9993

The rate of heavy metal pollution in some grape seed samples cultivated in Turkey were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES). Iron, zinc and copper were found high levels in the seed samples. The highest content in the majority was established as iron. On the contrary, cadmium and nickel were established low concentrations. The cadmium contents had markedly lower. The lowest and the highest cadmium concentrations were 0.12 ppm in the Göküzüm from Konya (Taskent) and 0.49 ppm Nazlı sample from Meram (Konya), respectively. Iron contents of grape seeds ranged from 21,65 ppm (Aküzüm) (Hatip-Konya) to 192.16 ppm (Göküzüm) (Taskent-Konya). In addition, Eksikara seed contained 140.45 ppm iron.

**Key Words:** Grape seeds, Locations, Heavy metals, ICP-AES.

### INTRODUCTION

There are many identified cultivars of grape grown in Turkey. Turkey has a very rich genetic potential in grapes due to varying climatic conditions and is one of the world's leading grape producers<sup>1,2</sup>. The large amount of grape seeds were obtained from processing of wine, vinegar and the other grape products. About the total production amounts of grape seeds is average 2-3 % of the grape production capacity (ca. 40 % grape production<sup>1</sup>).

The ecological importance of heavy metals has attracted a great deal of attention from governmental and regulatory bodies who are concerned in reducing the human health risk associated to the environmental pollution<sup>3</sup>.

Industrial uses of metals and other domestic processes have introduced substantial amounts of potentially toxic heavy metals into the atmosphere and into the aquatic and terrestrial environments<sup>4</sup>. For example, Turkey has an important potential source for rose, cornelian, wild plum and other minor fruits such as turpentine, hawthorn. Cadmium and lead are very harmful element for human body. For this reason, WHO and FAO determined the allowable maximum limit of cadmium in cereals and legumes as 0.5 ppm<sup>5</sup>. The increase in the consumption of refined foods and the lack of vitamins and minerals in the diet can cause health problems. Dietary supplements are widely utilized as a way to include essential vitamins and minerals in the diet<sup>6</sup>.

The aim of this work is to measure heavy metal contents of some grape seeds grown at the road sides polluted by vehicle emissions, industrial waste and uncontrolled factory emissions or possible sources of the heavy metal pollution.

### EXPERIMENTAL

Grape seeds were collected from vineyards growing in several locations of Konya in July, 2009 (Table-1). Each sample (ca. 1 kg) was collected from three different sides in the same harvest period. Fruits were cleaned by using dry air and crushed with the clean plastic spoon and dried at ambient temperature in air conditions. After drying, the seeds were removed from dried fruits and ground in a mill. The ground fruits were stored in 4 °C until the analyses. Map Info Professional 8.5 version of the map coordinates analysis with GIS mapping and analysis of data were made<sup>7</sup>.

**Determination of mineral contents:** About 0.5 g of dried seed samples was put into burnig cup with 15 mL of pure nitric acid. The sample was incinerated in a MARS 5 microwave oven at 200 °C. Distilled deionized water and ultrahigh-purity commercial acids were used to prepare all reagents, standards and samples. After digestion treatment, samples were filtrated through Whatman No. 42. The filtrates were collected in 50 mL flasks and analyzed by ICP-AES. The mineral contents of the grape seed samples were quantified against standard solutions of known concentrations which were analyzed concurrently<sup>8</sup>.

TABLE-1  
HEAVY METAL CONTENTS OF GRAPE SEEDS (dwt<sup>a</sup>)

No.	Common name	Locations	Heavy metals (ppm)				
			Cd	Cu	Fe	Ni	Zn
1	Çavus-beyaz	Konya	0.27 <sup>b</sup> ± 0.090 <sup>c</sup>	8.76 ± 1.12	33.45 ± 1.23	0.31 ± 0.040	8.89 ± 0.67
2	Ziraat Beyaz	Beybes-Konya	0.37 ± 0.030	12.01 ± 0.09	27.99 ± 2.34	0.33 ± 0.060	9.74 ± 0.45
3	Hesap ali	Hadim-Konya	0.34 ± 0.060	7.79 ± 0.08	60.74 ± 1.67	1.94 ± 0.090	12.71 ± 0.43
4	Keçimen	Beybes-Konya	0.47 ± 0.120	10.05 ± 1.03	28.11 ± 0.98	0.59 ± 0.020	6.78 ± 0.79
5	Aküzüm	Konya-Hatip	0.30 ± 0.050	5.70 ± 0.06	21.65 ± 0.59	0.40 ± 0.230	6.67 ± 0.87
6	Dökülgen	Konya-Kovanagzi	0.32 ± 0.040	12.78 ± 1.14	57.70 ± 1.37	1.96 ± 0.050	8.48 ± 1.03
7	Pekmezlik	Bozkir-Konya	0.23 ± 0.020	7.75 ± 1.07	32.88 ± 1.89	1.77 ± 0.070	7.18 ± 0.89
8	Ince kabuk	Hadim-Konya	0.30 ± 0.030	6.23 ± 0.23	49.75 ± 2.58	1.41 ± 0.090	8.29 ± 0.37
9	Kizil üzüm	Konya-Hatip	0.28 ± 0.010	9.14 ± 0.56	58.06 ± 3.67	0.93 ± 0.110	10.29 ± 0.78
10	Gök üzüm	Konya-Hatip	0.24 ± 0.020	8.86 ± 0.89	25.77 ± 0.89	2.92 ± 0.010	8.18 ± 1.05
11	Kizil üzüm	Bozkir-Konya	0.27 ± 0.060	10.02 ± 0.54	41.61 ± 1.43	2.79 ± 0.030	12.52 ± 0.98
12	Siyah erkek üzüm	Bozkir-Konya	0.30 ± 0.010	11.47 ± 0.34	25.63 ± 1.67	1.76 ± 0.080	12.73 ± 1.08
13	Sergi	Hadim-Konya	0.25 ± 0.070	9.93 ± 1.17	28.38 ± 2.37	1.42 ± 0.010	8.81 ± 0.37
14	Eksi kara	Hadim-Konya	0.36 ± 0.070	7.90 ± 0.57	140.45 ± 9.65	1.72 ± 0.320	12.14 ± 0.69
15	Topacik	Beysehir-Konya	0.37 ± 0.040	11.96 ± 0.69	37.06 ± 2.58	0.94 ± 0.280	6.30 ± 0.43
16	Pekmezlik	Alakovan-Konya	0.33 ± 0.110	8.05 ± 0.07	31.05 ± 3.89	1.35 ± 0.120	4.35 ± 0.23
17	Topacik	Konya- Beysehir	0.34 ± 0.090	16.42 ± 0.79	29.31 ± 0.98	2.86 ± 0.080	10.71 ± 1.28
18	Büzgülü	Konya-Hatip	0.26 ± 0.060	6.98 ± 0.37	31.18 ± 0.79	3.47 ± 0.090	7.12 ± 0.17
19	Nazli	Konya-Meram	0.49 ± 0.030	6.32 ± 0.54	24.18 ± 0.37	2.61 ± 0.030	3.76 ± 0.03
20	Karadimrit	Hadim-Konya	0.35 ± 0.012	6.23 ± 0.43	22.04 ± 0.58	2.31 ± 0.050	3.14 ± 0.06
21	Misket	Hadim-Konya	0.28 ± 0.030	6.65 ± 0.12	73.81 ± 2.76	0.43 ± 0.010	10.64 ± 0.36
22	Isbitiren	Hadim -Konya	0.20 ± 0.090	11.61 ± 1.28	28.32 ± 1.23	0.82 ± 0.010	12.71 ± 0.42
23	Göküzüm	Taskent -Konya	0.12 ± 0.010	13.24 ± 0.38	192.16 ± 8.79	0.88 ± 0.240	13.62 ± 0.54
24	Irikara	Taskent-Konya	0.33 ± 0.013	12.77 ± 0.67	59.24 ± 3.46	0.80 ± 0.020	11.01 ± 1.37
25	Isbitiren	Taskent-Konya	0.32 ± 0.090	11.15 ± 0.87	70.18 ± 3.89	1.20 ± 0.060	13.24 ± 1.29
26	Dimrit	Taskent-Konya	0.37 ± 0.070	8.66 ± 1.28	85.50 ± 5.67	0.78 ± 0.011	10.01 ± 0.89
27	Muftalma	Taskent-Konya	0.40 ± 0.030	11.23 ± 1.29	24.73 ± 1.27	0.53 ± 0.070	10.81 ± 1.33

<sup>a</sup>Dry weight; <sup>b</sup>Mean; <sup>c</sup>Standard deviation.

Working conditions of ICP-AES: Instrument: ICP-AES (Varian-Vista); RF power : 0.7-1.5 kw (1.2-1.3 kw for Axial); Plasma gas flow rate (Ar): 10.5-15 L/min (radial) 15 " (axial); Auxiliary gas flow rate (Ar): 1.5 " ; Viewing height: 5-12 mm; Copy and reading time: 1-5 s (max. 60 s); Copy time: 3 s (max. 100 s).

**Statistical analyses:** Results of the research were analyzed for statistical significance by analysis of variance<sup>9</sup>. This research was performed by three duplicates with a replicate.

## RESULTS AND DISCUSSION

The composition in heavy metals in grape seeds collected from different locations are given Table-1. Iron content of seeds was found at the high levels. On the contrary, Cd and Ni were found low concentrations. The Cd contents were markedly lower.

The lowest and the highest cadmium concentrations were 0.12 ppm in the Göküzüm from Konya (Taskent) and 0.49 ppm Nazli sample from Meram (Konya), respectively. The lowest copper content was 5.70 ppm in the Aküzüm sample of Hatip (Konya) (Table-1). Iron contents of grape seeds ranged from 21.65 ppm (Aküzüm) (Hatip-Konya) to 192.16 ppm (Göküzüm) (Taskent-Konya) in the grape seed samples. In addition, Eksikara seed contained very high Fe (140.45 ppm). The Çavusbeyaz grape seed from Konya (0.31 ppm) had the lowest nickel content, while the highest Ni content was 3.47 ppm in the Büzgülü grape seed sample from Konya (Hatip). Zinc contents of grape seed samples changed between 3.14 ppm (Karadimrit) to 13.62 ppm (Göküzüm). Generally, Cu,

Fe and Zn contents of grape seeds were found high when compared with results of Cd and Ni. However, average cadmium levels were found similar with results reported by Göktangolar *et al.*<sup>2</sup>. The zinc level in the grape seeds was found low than those of reported by Göktangolar *et al.*<sup>2</sup>. In this study, iron, quantitatively, was the most abundant toxic metal compared to other metals tested. Possible interpretation of this amount might be that the grape fruits may be contaminated by processing equipment during the processing of grapes. Also, the reason might be that the industry has been well developed in this area.

Among heavy metals, cadmium(II) plays a major role. Its presence is due to the growing use of sewage sludge's and other wastes in agricultural lands<sup>10</sup>. Cadmium(II) is absorbed by plants and enters the food chain. In human being, it is permanently retained owing to its metabolic inertness and may cause severe problems to human health<sup>11</sup>. The daily requirements of an adult man are as follows ( mg/d): 10-15 Fe, 12-15 Zn and 2-3 Cu<sup>12-14</sup>. The limited edible portion of numerous fruits also limits their interest as nutrient sources. Many of them have a thick skin and large seeds or a large number of seeds<sup>15</sup>. FA/WHO fixed an allowable daily intake of cadmium(II) of 7 mg/kg of body weight<sup>11</sup>. Zinc(II) is an essential metal for human body in minimal amounts, whereas it is dangerous in higher quantities<sup>16</sup>; Cadmium exposure cause chromosome aberration, cancer and birth defects<sup>17</sup>; the main sources of these element are the combustion of fuel, industrial emissions, varnishes and chemical colorants<sup>18</sup>. Some micronutrients as copper and zinc, are essential for plant growth and human nutrition at low doses

but may also be toxic for humans, animals and plant at high doses<sup>19</sup>.

The results showed that the grape seeds from different locations and altitudes were generally correlated with the degree of heavy metal contamination of the soil, fertilizers, processing equipment and environment.

### ACKNOWLEDGEMENTS

This work was supported by Selçuk University Scientific Research Project (S.U.-BAP, Konya, Turkey).

### REFERENCES

1. S. Çelik, Bağcılık (Ampeloloji) Cilt 1. Sti: Anadolu Matbaa Ambalaj San. ve Tic. Ltd. p. 426 (1998).
2. S. Göktangolar, Y. Özogul, S. Tangolar and A. Torun, *Int. J. Food Sci. Nutr.*, **60**, 32 (2009).
3. O. Morton-Bermea, E. Hernández-Álvarez, G. González-Hernández, F. Romero, R. Lozano and L.E. Beramendi-Orosco, *J. Geochem. Exp.*, **101**, 218 (2009).
4. D.W. O'Connell, C. Birkinshaw and T.F. O'Dwyer, *Biores. Technol.*, **99**, 6709 (2008).
5. G. Jansson, Cadmium in Arable Crops, Doctoral Thesis, Swedish University of Agricultural Sciences, Uppsala (2002).
6. M. Ivey and G. Elmen, Nutritional Supplement, Mineral and Vitamin Production in: Handbook of Non-prescription Drugs, American Pharmaceutical Association, The National Professional Society of Pharmacists, 2215 Constitution Avenue, N.W. Washington, DC 20037, USA, edn. 8, p. 215 (1986).
7. Anonymous, Available In: <http://maps.google.com/>(2010).
8. S. Skujins, Handbook for ICP-AES (Varian-Vista). A Hort Guide To Vista Series ICP-AES Operation, Varian Int. AGsZug, Version 1.0, Switzerland, p 29 (1998).
9. H. Püskülcü and F. İkiz, Introduction to Statistic, Bilgehan Press, Bornova, Izmir, Turkey, p. 333 (1989) (in Turkish).
10. F. Lo Coco, L. Ceccon, L. Ciralo and V. Novelli, *Food Control*, **14**, 55 (2003).
11. N.T. Crosby, *The Analyst*, **102**, 225 (1997).
12. C. Berdanier, Advanced Nutrition: Micronutrients, Boca Raton: CRC Press (1998).
13. L. Smolin and M. Grosnevor, Nutrition: Science and applications, Orlando: Haecourt College Publishers, edn. 3 (2000).
14. R. Wildman and D. Mederios, Advanced Human Nutrition. Boca Raton: CRC Press (2000).
15. P. Leterme, A. Buldgen, F. Estrada and A.M. Londono, *Food Chem.*, **95**, 644 (2006).
16. M. Choudhary, L.D. Bailey, C.A. Grant and D. Leisle, *Can. J. Plant Sci.*, **75**, 445 (1995).
17. R.B. Heyes, *T Canc. Causes Cont.*, **8**, 371 (1997).
18. E. Rojas, L.A. Herrera, L.A. Poirier and P. Ostrosky-Wegman, *Mutat. Res.*, **443**, 157 (1999).
19. M.J. McLaughlin, D.R. Parker and J.M. Clarke, *Field Crop Res.*, **60**, 143 (1999).