

## EVALUATION OF THE MINERAL ELEMENT PROFILE OF WASTES OF SOME WINE GRAPE (*VITIS VINIFERA* L.) VARIETIES

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### ABSTRACT

In this study, the level of macro and micro elements of six wine grape cultivars were determined in seeds, bagasse (skin and pulp) and pomace (seed, skin and pulp) by inductively coupled plasma mass spectrometry and atomic absorption spectroscopy after microwave digestion (ICP-AES). The levels of macro and micro elements exhibited a genotype dependent alteration and affected by the part of the berry sampled. Potassium was the predominant macro element in bagasse and pomace, varying from 6.78 g/kg dry weight in pomace (Carignane) to 21.05 g/kg dry weight in bagasse (Cabernet Sauvignon). However, the level of calcium was higher than potassium in seeds and varied between 4.95 g/kg (Kalecik karası) and 6.73 g/kg (Carignane). Seeds were also richer than the bagasse and pomace related with phosphorus, magnesium, and sulfur. Among the micro elements, Fe had the highest amount in all parts of the berries. Its content ranged from 13.9 mg/kg dry weights in bagasse of Semillon to 24.8 mg/kg dry weight in seeds of Syrah. Iron, manganese, zinc and molybdenum in seeds; copper and boron in bagasse were higher amount than the other groups analyzed. The results of this study show that all parts of the grape berries are potentially rich sources of mineral elements. So, they could be used as a food supplement to improve the nutritive value of the human diet and for some engineering processes in food industry.

**Keywords:** Grapevine, Wine Grape, Mineral Elements, Grape Wastes, Bagasse, Pomace

Received: 11.01.2018  Accepted: 07.02.2018  Published: 15.03.2018

### INTRODUCTION

Wine grape production has an important amount in total grape production of the world. Annual world grape production is 73.5 million metric tons. Approximately, 70% of this total belongs to wine grape production [1]. Yearly world wine production is about 30 billion liters.

In Turkey, about 38% of the total grape production which is four million tons is used for raisins, 50% used as table, and 12% used for winemaking and the production of grape juice, jam, jelly and other traditional grape products (such as molasses, vinegar, etc.) [2, 3, 4, 5].

Besides Turkey, in the entire wine producing countries, wine and grape juice industries have been producing an important amount of grape waste and by products [6,7, 8, 9]. Some of these are grape seeds, stalks, skin and pulp. Totally, more than 20 percent of clusters of wine grapes are obtained as waste. Management of grape wastes is one of the important problems for wine and the other grape juice industries. Researches have been

going on for obtaining high quality products such as compost, fertilizer, grapeseed oil etc. from grape wastes [6, 10, 11].

Recent studies have shown that grapes and their wastes have many benefits on human health, such as those coming from carbohydrates, sugar, organic acids, soluble and insoluble fiber, vitamins (A, B, C, and E), fatty acids, amino acids, polyphenols (flavonoids, phenolic acids, and resveratrol) and most of the macro and micro minerals (calcium, potassium, magnesium, boron, manganese and iron etc. [2, 12, 13, 14, 15, 5, 9, 11, 16, 17, 18, 19]. Daily consumption of grapes and grape products has been recommended in articles [20, 15].

However, there is a lack of knowledge on the utilization of wine and grape juice industry wastes for food industry, the utilization of these wastes in the food industry can create new food sources for human consumption, and create additional markets for grape producers [6, 8, 11, 19].

The objective of this study was to investigate the macro and micro element constituents of grape berries of eight wine grape cultivars.

## MATERIALS AND METHODS

### Materials

This experiment was carried at an experimental vineyard, established in approximately 1100 m elevation from sea level in Pozantı/Adana Research Station of Cukurova University on a clayey loam soil. Wine grape varieties used were Kalecik karası, Syrah, Carignane, Semillon, Chardonnay and Cabernet Sauvignon.

The own rooted grapevines were 18 years old and trained on bi-lateral cordon trellis system with three wires (one wire for the arms and two wires for the foliage) at 1.3 m canopy height and spur pruned. Planting distances were 2 m × 3 m (vine × row) in west-east row orientation. Vineyard was under non-irrigated and without manure conditions. Suckering was done before flowering and shoot trimming was achieved after fruit set. All other practices were applied according to the standard viticultural practices.

Thirty vines of each variety were arranged in three replications of 10 vines each. Total thirty clusters (10 clusters from each replication) were randomly sampled from vines at harvest time of each cultivar. Brix level was 22 for Carignane, 23 for Cabernet Sauvignon, 24.5 for Shiraz and Semillon, 25.5 for Kalecik karası and 26.5 for Chardonnay. Berries were separated from clusters without pedicels and these were squeezed by hand through cheesecloth. After removing the juice, the rest were separated into groups for analysis, as seeds and bagasse (skin and pulp). Samples were held at 65 °C to constant weight in a drying oven and dried samples were ground in a plant grinder. They were stored at -80 °C until analyzed.

### Methods

Elemental concentration for macro (P, K, Ca, Mg, S, Na) and micronutrients (Fe, Cu, Zn, Mn, Mo, B) were analyzed as follows. Ground berry samples were subjected to acid digestion in a closed microwave system (Milestone 1200 Mega) by using 1 ml of 30% H<sub>2</sub>O<sub>2</sub> and 5 ml of 65% HNO<sub>3</sub>. Elemental concentrations of the digested samples were measured by ICP–AES (Inductively Coupled Plasma-Atomic Emission Spectrometry, Jobin Yvon-Paris). Elements concentration was checked by using certified standard reference

materials from the National Institute of Standards and Technology (NIST; Gaithersburg, MD).

### Statistical analyses

One-way analysis of variance using a completely randomized design was performed on the data using the MSTAT-C statistics program. The means presented in the tables with a standard error of the mean consist of three replications. Differences between the means were obtained by the LSD (Least Significant Difference) test at 1% level [21, 22].

## RESULTS

**Bagasse (skin and pulp):** Macro and micro element contents of bagasse are presented in Table 1. Among the macro elements, the level of potassium was found to be higher than the other elements. Potassium content of bagasse was between 7.87 g/kg for Carignane and 21.05 g/kg for Cabernet Sauvignon. In this part of berry, after potassium, calcium levels ranged from 1.00 to 1.70 g/kg, phosphorus from 0.83 to 1.19 g/kg, sulfur from 0.47 to 0.75 g/kg, magnesium from 0.39 to 0.61 g/kg, and sodium from 0.02 to 0.08 g/kg.

Among the micro elements iron was the predominant element in bagasse of grapes. This element was followed by copper, manganese, zinc, and the others, respectively. The micro elements level of bagasse ranged from 13.9 (Semillon) to 23.1 mg/kg (Chardonnay) for iron, from 5.2 (Semillon) to 18.4 mg/kg (Cabernet Sauvignon) for copper and from 3.6 (Semillon) to 10.9 mg/kg (Cabernet Sauvignon) for manganese, from 2.6 (Semillon) to 4.7 mg/kg (Cabernet Sauvignon) for zinc.

**Seeds:** Macro and micro element contents of seeds are presented in Table 2. Among the macro elements, the calcium contents of seeds were found to be higher than the other elements. The calcium level of seeds varied between 4.95 g/kg (Kalecik karası) and 6.73 g/kg (Carignane). This element was followed by potassium, phosphorus, magnesium, sulfur and sodium elements level, respectively. The highest levels of macro elements of seeds were found in Kalecik karası and Cabernet Sauvignon for potassium, in Cabernet Sauvignon for magnesium, in Syrah for phosphorus, in Carignane and Chardonnay for sulfur, and both of the Semillon and Chardonnay for sodium.

Among the micro elements iron had the highest amount in seeds of the berries, similar to bagasse levels. There were no significance differences among cultivars for lead levels of seeds. Iron, manganese, copper and zinc contents of seeds were higher than that of the other micros.

The micro element content of seeds ranged from 17.6 (Semillon) to 24.8 (Syrah and Chardonnay) mg/kg for iron, from 9.2 (Semillon) to 12.7 (Chardonnay) mg/kg for copper, from 12.0 (Kalecik karası) to 26.6 (Cabernet Sauvignon) mg/kg for manganese, from 9.9 (Kalecik karası) to 14.3 (Chardonnay) mg/kg for zinc, from 0.09 (Semillon) to 0.24 (Cabernet Sauvignon) mg/kg for boron, from 0.08 (Kalecik karası) to 0.50 (Syrah) mg/kg for Molybdenum.

**Pomace (seed, skin and pulp):** Macro and micro element contents of pomace are presented in Table 3. Among the macro elements, the level of potassium was found to be higher than the other elements. The highest levels were obtained from Cabernet Sauvignon for potassium (17.6 g/kg), from Syrah (3.46 g/kg) and Carignane for calcium (3.27 g/kg), from Syrah for phosphorus (1.91 g/kg), from Cabernet Sauvignon for sulfur (0.93 g/kg), from Carignane and Cabernet Sauvignon for magnesium (0.85 g/kg) and from Semillon for sodium (0.07 g/kg).

Among the micro elements iron had also the highest amount in pomace of the berries. This element was followed by copper, manganese, zinc, and the others, respectively. Except for iron, there were significant differences among the cultivars for all the micro elements level of pomace. Iron levels have varied between 14.1 (Semillon) and 23.9 mg/kg (Carignane). The highest and lowest values were obtained from Cabernet Sauvignon and Semillon (15.7 and 6.2 mg/kg, respectively) for copper, from Cabernet Sauvignon and Semillon (14.5 and 6.6 mg/kg, respectively) for manganese, from Syrah and Semillon (7.53 and 4.0 mg/kg, respectively) for zinc related with analysis of pomace.

## DISCUSSION

Macro and micro elements values found in our research for grape pomace and seeds and bagasse fractions were evaluated as considerable amounts for all varieties. Although there are many literature on the mineral contents of whole grapes [12, 13,

23, 14, 5, 24, 16], knowledge on comparing the mineral levels in different parts of the berries is lacking. So, this article has been discussed using limited reports.

Tangolar et al. [11] reported that macro and micro element values of grape seeds were changed between 2.9 and 4.4 g/kg for phosphorus; 3.3 and 5.0 g/kg for potassium; 1.3 and 1.7 g/kg for magnesium; 4.8 and 7.9 g/kg for calcium and 12.28 and 18.97 mg/kg for zinc; 17.30 and 27.0 mg/kg for iron; 11.13 and 23.86 mg/kg and 7.27 and 13.04 mg/kg for copper in their research. These results were in agreement with the results from in our study. Macro and micro elements values in berries from healthy, symptomatic and asymptomatic vines obtained by [25] were also very close to the bagasse and pomace values.

Similarly, the potassium values in this study were close to the values of [13, 23, 5, 24, 17] given for about 1 kg of grapes. Besides these grape values, according to the [26], potassium values were also about 8-12 g/kg for dry beans, 7-7.1 g/kg for nuts, 4-4.25 g/kg for potato, 2-2.1 g/kg for orange and 1.0-1.1 g/kg for apple. These results showed that, potassium level of berry parts apart from grape juice were found to be remarkably similar amounts. Similarly, the sodium values were found close to the values reported in the same literature, but calcium, magnesium, copper, iron and zinc values given in this report were lower than those in our study. This is because, berry parts other than fruit juice is thought to be a result of being more intense. Iron amounts were a little less than the amounts given by [26] for the legumes, but higher than that of potatoes, oranges and apples.

Macro and micro element level in different fruits and vegetables given [23] have also clearly shown the importance of nutrient capacity in different parts of the grapes. These, demonstrated that the seed, skin and pulp of the berries (in other words "wastes and by-products of grape juice or wine making industry) could be used as a rich mineral elements source.

Finally, it can be explained that wastes obtained from wine making and grape juice industry are good natural sources of macro and micro elements. If they can be used as a food supplement to improve the nutritive value of the human diet and industrial purposes, they will be very beneficial to human nutrition and the food industry.

**Table 1.** Macro and micro element contents of bagasse (skin and pulp)

Cultivar	Macro elements (g/kg dry weight)					
	P	K	Mg	Ca	S	Na
Syrah	1.08±0.05 b	9.33±0.40 d	0.40±0.01 de	1.25±0.02 c	0.64±0.01 b	0.02±0.00 d
Kalecik karası	0.90±0.01 c	10.2±0.2 c	0.41±0.00 d	1.57±0.02 b	0.58±0.00 c	0.03±0.00 d
Carignane	0.83±0.00 c	7.87±0.04 e	0.61±0.01 a	1.70±0.04 a	0.47±0.01 f	0.04±0.01 cd
Semillon	0.90±0.01 c	8.92±0.10 d	0.39±0.00 e	1.00±0.02 e	0.52±0.00 d	0.08±0.00 a
Chardonnay	0.89±0.00 c	10.98±0.02 b	0.49±0.00 c	1.05±0.00 de	0.50±0.00 e	0.06±0.00 ab
Cabernet Sauvignon	1.19±0.01 a	21.05±0.10 a	0.53±0.00 b	1.10±0.01 d	0.75±0.00 a	0.05±0.00 bc
LSD 1%	0.06	0.57	0.02	0.07	0.01	0.02
Cultivar	Micro elements (mg/kg dry weight)					
	Fe	Cu	Mn	Zn	B	Mo
Syrah	18.3±0.9 ab	7.3±0.1 b	4.2±0.1 d	3.5±0.2 b	0.31±0.02 d	0.23±0.01 a
Kalecik karası	19.6±0.02 ab	6.7±0.06 b	5.6±0.04 c	3.1±0.27 b	0.39±0.00 c	0.13±0.02 b
Carignane	15.2±0.6 b	5.8±0.5 c	6.4±0.1 b	3.2±0.4 b	0.37±0.0 c	0.02±0.0 c
Semillon	13.9±0.02 b	5.2±0.02 c	3.6±0.05 e	2.6±0.04 b	0.36±0.00 c	0.12±0.01 b
Chardonnay	23.1±3.3 a	5.9±0.05 c	4.1±0.00 d	2.8±0.05 b	0.47±0.00 b	0.04±0.01 c
Cabernet Sauvignon	18.9±0.44 ab	18.4±0.2 a	10.9±0.05 a	4.7±0.08 a	0.86±0.00 a	0.11±0.03 b
LSD 1%	4.4	0.7	0.2	0.7	0.03	0.06

Mean values (n: 3) followed with one or more of the same letters in the each column were not significantly different at  $P < 0.01$ , according to the LSD test; Elements are analyzed separately.

**Table 2.** Macro and micro element contents of grape seeds

Cultivar	Macro elements (g/kg dry weight)					
	P	K	Mg	Ca	S	Na
Syrah	3.22±0.03 a	3.75±0.04 b	1.30±0.02 d	6.54±0.06 a	1.25±0.01 b	0.04±0.02 ab
Kalecik karası	2.33±0.02 d	4.73±0.03 a	1.29±0.01 d	4.95±0.02 c	1.12±0.01 d	0.01±0.00 b
Carignane	3.05±0.03 b	3.87±0.01 b	1.42±0.01 c	6.73±0.04 a	1.32±0.01 a	0.05±0.00 ab
Semillon	2.35±0.02 d	3.10±0.03 c	1.30±0.01 d	6.32±0.02 b	1.17±0.01 c	0.06±0.00 a
Chardonnay	2.91±0.03 c	3.83±0.04 b	1.47±0.02 b	6.27±0.08 b	1.30±0.02 a	0.06±0.00 a
Cabernet Sauvignon	2.41±0.02 d	4.74±0.06 a	1.63±0.01 a	6.26±0.02 b	1.23±0.01 b	0.04±0.01 ab
LSD 1%	0.07	0.01	0.04	0.18	0.03	0.03
Cultivar	Micro elements (mg/kg dry weight)					
	Fe	Cu	Mn	Zn	B	Mo
Syrah	24.8±1.04	12.1±0.12 b	19.2±0.3 b	13.8±0.10 b	0.11±0.00 d	0.50±0.03 a
Kalecik karası	23.2±3.6	9.8±0.07 d	12.0±0.09 d	9.9±0.03 e	0.16±0.00 b	0.08±0.00 d
Carignane	23.6±0.1	10.9±0.01 c	19.2±0.2 b	13.2±0.4 c	0.13±0.00 c	0.11±0.01 d
Semillon	17.6±0.2	9.2±0.01 e	17.1±0.2 c	10.4±0.03 e	0.09±0.01 e	0.35±0.00 b
Chardonnay	24.8±0.3	12.7±0.2 a	17.3±0.2 c	14.3±0.2 a	0.13±0.00 c	0.19±0.02 c
Cabernet Sauvignon	20.5±0.3	12.5±0.1 a	26.6±0.1 a	12.0±0.1 d	0.24±0.00 a	0.23±0.04 c
LSD 1%	NS	0.30	0.52	0.52	0.01	0.07

Mean values (n: 3) followed with one or more of the same letters in the each column were not significantly different at  $P < 0.01$ , according to the LSD test; Elements are analyzed separately. NS. Non-Significant

**Table 3.** Macro and micro element contents of pomace (seed, skin and pulp)

Cultivar	Macro elements (g/kg dry weight)					
	P	K	Mg	Ca	S	Na
Syrah	1.91±0.08 a	7.09±0.16 de	0.75±0.03 b	3.46±0.25 a	0.88±0.03 b	0.05±0.02 ab
Kalecik karası	1.44±0.01 bc	8.34±0.01 c	0.73±0.00 b	2.64±0.02 b	0.78±0.00 c	0.02±0.00 b
Carignane	1.46±0.07 bc	6.78±0.08 e	0.85±0.01 a	3.27±0.12 a	0.72±0.02 d	0.02±0.00 b
Semillon	1.23±0.00 d	7.29±0.09 d	0.61±0.01 c	2.35±0.03 b	0.67±0.00 d	0.07±0.00 a
Chardonnay	1.32±0.01 cd	8.87±0.04 b	0.73±0.01 b	2.48±0.03 b	0.70±0.01 d	0.05±0.01 ab
Cabernet Sauvignon	1.59±0.01 b	17.6±0.17 a	0.85±0.00 a	2.66±0.03 b	0.93±0.00 a	0.05±0.00 ab
LSD 1%	0.14	0.33	0.05	0.36	0.05	0.02
Cultivar	Micro elements (mg/kg dry weight)					
	Fe	Cu	Mn	Zn	B	Mo
Syrah	20.5±1.0	9.7±0.3 b	10.1±0.6 b	7.53±0.4 a	0.22±0.01 e	0.32±0.03 a
Kalecik karası	21.0±1.9	7.7±0.02 c	7.3±0.1 c	5.13±0.02 c	0.31±0.0 c	0.14±0.04 bc
Carignane	23.9±7.7	7.0±0.2 d	10.7±0.5 b	6.07±0.6 bc	0.30±0.00 c	0.08±0.02 c
Semillon	14.1±0.1	6.2±0.1 e	6.6±0.1 c	4.00±0.1 d	0.27±0.01 d	0.15±0.02 bc
Chardonnay	16.6±0.2	7.4±0.02 cd	7.4±0.1 c	5.40±0.1 c	0.38±0.0 0b	0.08±0.03 c
Cabernet Sauvignon	19.7±0.6	15.7±0.1 a	14.5±0.2 a	6.87±0.1 ab	0.74±0.01 a	0.23±0.04 ab
LSD 1%	NS	0.5	1.0	0.9	0.02	0.09

Mean values (n: 3) followed with one or more of the same letters in the each column were not significantly different at  $P < 0.01$ , according to the LSD test; Elements are analyzed separately. NS. Non-Significant

## CONCLUSIONS

Wineries and other grape juice processing industry have been producing important amount of grape wastes every year and after the processing to different ways, it's by –products have especially been using as compost in grape growing and the other areas. Seeds are important part of grape pomace and from this very valuable grapeseed oil is produced. So in this experiment seeds were also evaluated separately. This work is aimed to show the amount of macro and micro nutrients to be gained using with/ or without seed of grape pomace. It was shown that seeds for phosphorus, magnesium, calcium, sulfur, iron, manganese, zinc and for molybdenum; bagasse for potassium, copper, and for boron was considerable rich sources. This source can also be evaluated to increase the food value.

## ACKNOWLEDGEMENT

The authors thank Academic Research Unit of Çukurova University for the financial support provided for this study (Project number: AMYO2009BAP4).

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