https://dergipark.org.tr/tr/pub/food
OPEN ACCESS JOURNAL

ISSN 2667-5803

FHTI Journal of Food Health and Technology Innovations
September Vol 2, No 5 (2019)

DergiPark AKADEMİK

Research Article

The Effects of Clinoptilolite on Mineral Substance of Raising in Organic Grape Growing

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This Proceeding Paper was Presented as Oral Presentation at '9th International Soil Science Congress on "The Soul of Soil and Civilization", 14-16 October 2014 , September 28-29, 2018, Side, Antalya

Abstract

This study was carried out in Alaşehir-Yeşilyurt Enterprise of Manisa Viticulture Research Institute in the western part of Turkey from 2006 to 2007. The objective of this study was to determine the influence of an applied clinoptilolite on mineral substance analyses of organically grown Sultani Çekirdeksiz grape variety were investigated. Experiments were undertaken using randomized block design with three replicates consisting of 12 vines per parcel. Mineral substance analyses of the raisins obtained from the applications were performed using the ICP-AES technique. It was found that there was an increase in average potassium (K), magnesium (Mg), zinc (Zn) calcium (Ca) and phosphorus (P) contents and a decrease in copper (Cu) contents application of clinoptilolite as compared to control and a difference of 5% was determined between applications.

Key words: Mineral substance, organic grape, raisins, Sultani Çekirdeksiz

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Introduction

Turkey, located in most convenient climate zone in the world for viticulture, has a longstanting and long-established viniculture culture and a rich grapevine gene potential due to its location in the center of the geography where the gene centers intersect. (Çelik, 1998).

Having an important place in world viniculture industry, viniculture of Turkey one of the important agricultural branches in terms of breeding area, amount of production and income.

Grape is a valuable product that has a significant place in the agriculture of Turkey with its diversity of evaluation forms, domestic market consumption and export share, and thus constitutes the area of activity and direct income of a large farmer's sector.

Turkey is among the largest grapevine growing countries of the world with approximately 468,792 hectares of vineyard area and 4.01 million tons of grape production (5th in area; 6th in production). Grape production mainly consists of 52.8% table grapes, 36.4% raisins and 10.8% must-wine varieties (Anonymous, 2018).

Organic agriculture is a system for crops, livestock and fish farming that emphasizes environmental protection and the use of natural farming techniques. It is concerned not only with the end-product, but with the entire system used to produce and deliver the agricultural product. To this end, the entire farm cycle, from production and processing, to handling and delivery, excludes the use of artificial products such as genetically modified organisms (GMOs) and certain external agricultural inputs such as pesticides, veterinary drugs, additives and fertilizers. Organic farmers rely instead on natural farming methods and modern scientific ecological knowledge in order tomaximize the long-term health and productivity of the ecosystem, enhance the quality of the products and protect the environment. Proponents of organic methods believe that it is a more sustainable and less damaging approach to agriculture (Morgera et al.2012).

In the world, organic grapes are grown in 379 555 hectares and this constitutes 5.3 %of the world's grape growing area. Turkey is a major grape producer in the world. Since 1985, Turkey producing and exporting organic raisins is a world leader in the production of raisins. Vineyards where organic grapes are grown are generally located in the provinces of Izmir and Manisa, and almost all the grapes are dried and exported to European countries in particular. In Turkey, 13 961 hectares grape are grown organically which constitutes 3.2 % of the total grape production area (Willer and Lernoud, 2019).

Processed as both table grapes and raisins, Sultani Çekirdeksiz grape variety is one of the most important export products of the country. Sultani Çekirdeksiz grapes variety is mostly grown using conventional methods in the Aegean Region. Of late years, however, it has been observed that companies of European origin have been making contracts with growers for organic grape production through their agencies in Turkey, which increases production based on organic methods.

A total of 95.89 % of the organic Sultani Çekirdeksiz raisin producers and % 95.55 of the total production area for organic seedless raisins are found in Izmir and Manisa region. According to records of Aegean Exporters Unions, the income earned from organic seedless raisin exports was approximately 3 million $ in 1977; whereas this figure escalated 79 % and reached 5,257,629 $ in 2004 (Kenanoglu Bektaş and Milan, 2006).

According to Considine and Considine (1982) and also to Fidan and Yavaş (1986), mineral substances found in grape are taken up from the soil by the vine and transferred to the plant and the fruit. Although their quantities are within certain limits, they can vary depending on the variety of the grape, degree of ripeness, soil type, fertilizing and climatic conditions. Generally, the quantities of mineral substances are relatively lower in dry climates and during dry years. The quantities of mineral substances are affected by soil conditions; however, certain elements are influenced by atmospheric conditions and some others by plant protection drugs used for plant diseases and pests. The amount of iron in grapes is directly influenced by the iron content of the vineyard soil. Although content of copper is at significant levels in grapes, it tends to increase in cases where certain pesticides are used.

In their study in which they observed quantities of macro-elements and micro-elements in must made from three Hungarian grape varieties during the course of ripening, Diófási et al. (1986) stated that there was a positive correlation between the sugar quantity and N, P, Ca, Fe, and Mg elements.

In a study conducted by Adamian (1988) comparing substance contents of local Armenian, Western European and Central European table grape varieties, it was reported that Armenian grapes contained more mineral substances and had a higher Fe/Mn ratio; temporary varieties (seeded and seedless) contained more mineral substances compared to early-ripening varieties; and seedless early-ripening varieties contained more Cu and Mn that seeded ones.

Švejear and Okáč (1989) reported that amounts of Fe, Zn, Mn and Cu found in the grape and the wine were not only dependent on the presence of these minerals in the soil and that the composition of the soil, pH as well as climatic conditions were also important factors.

Boselli et al. (1995) stated there was a positive correlation between the pH in the grape must and the K content, and that pH in the must and K content could be affected by the rootstock used in a particular vineyard.

Aykut (2002) determined mineral substances found in musts of Seedless Sultana, Muscat Hamburg and Alicante Bouschet grape varieties in mg/kg as 1540-1750-1255 for K, 24-29.06-34 for Ca, 100-53.75-102.5 for Mg, 53.30-31.32-52.15 for Na, 136.9-97.20-168.2 for P, 1.88-0.71-1.38 for Fe, 2.5-1.69-0.8 for Cu, 0.68-0.79-0.35 for Zn ve 0.80-0.49-1.45 for Mn, respectively.

The mass of the human body is made up approximately 50 elements (Keskin, 1981). Twelve of these elements (O, C, H, N, Ca, P, K, S, Na, Cl, Mg and Fe) constitute 99.9 % of the total. Almost 99% of this ratio is O, C, H, N, Ca and P. These twelve elements are referred to as macro or quantitative elements, whereas the remaining ones are called micro or trace elements. Microelements are substances found in human body and nutrients in concentrations of less than 0.005 % (Keskin, 1981; Gözükara, 1990).

Raisins (*Vitis vinifera* L.) have been a favorite food since 1490 BC due to their nutritive value and high micronutrients content (Witherspoon, 2000). It was one of the most important and popular dried fruits in the world because their high nutritional value (Fang et al., 2010). Raisins should be of particular interest in these investigations due to their unique phytochemical composition and the natural qualities that make raisins an appealing source of necessary minerals including potassium, iron, vitamin B, calcium, magnesium, sodium, arsenic, cadmuim, chromium, manganese and nickel (Simsek et al., 2004; Fang et al., 2010).

In recent years, attention is paid to development of sustainable agriculture and hence the natural minerals as soil amendments are applied to improve physical and chemical properties soil (Abdi et al, 2006) . The great effectiveness of zeolites as natural sources of trace elements supplementing NPK and its high adsorption ability have been reported (Kolyagin and Kucherenko, 2003). Natural zeolites are used extensively in Japan as amendments for sandy, clay-poor soils. The pronounced selectivity of clinoptilolite $NH4^{++}$ and K^{+} also was exploited in slow-release chemical fertilizers (Minato, 1968). By using clinoptilolite-rich tuff as a soil conditioner, significant increases in the yields of wheat (13-15%), eggplant (19-55%), apples (13-38%) and carrots (63%) were reported when 4-8 ton acre zeolite was used (Mumpton, 1999). The addition of clinoptilolite also increased yields of barley, potato, clover and wheat after adding 15 t ha^{-1} to Ukrainian sandy loam soils (Mazur et al., 1986). Clinoptilolite amended to a potting medium for chrysanthemums behaved like a slow-release K-fertilizer, yielding the same growth for the plants as daily irrigation with Hoagland's solution (Hershey, 1980)

The present study was conducted on Sultani Çekirdeksiz grape variety, which has an important place in our national economy. The objective of this study was to determine the influence of an applied clinoptilolite on mineral substance analyses of the raisins. Raisins produced from Sultani Çekirdeksiz grape variety in organic grape parcels during organic production phase (2006-2007). Moreover, the study tries to emphasize the importance of raisins, organic raisins in particular, as a natural source of energy in human nutrition.

MATERIALS and METHODS

Experimental site

Field experiments were conducted from 2006 to 2007 in Alaşehir-Yeşilyurt Enterprise of Manisa Viticulture Research Institute in the western part of Turkey (38°20′N, 28°38′W). The area has a transition towards a continental climate from a Mediterranean climate. The annual average temperature of 16.7 ^{0}C and a mean annual rainfall of 598 mm, The summer months, including the harvest period, are quite hot with mean temperatures of 30 ^{0}C.

Experiments were planned as randomized block design with three replicates which were established in15 years old Sultani Çekirdeksiz vineyard under irrigable soil conditions and trained to "T" wire grape trellis training system and can-pruned to 60 buds per vine. The vines had between-row and within-row spacing of 3.3 and 2.4 m, respectively in organic parcel.

Sultani Çekirdeksiz is such a variety that it ripens in midseason. It grows strong with conical clusters, wings, normal density, small oval shaped berries and average berry skin thickness. Although it is a variety for drying, Sultani Çekirdeksiz is also consumed as table grapes through a series of culture practice.

Soil Composition of the Trial Vineyard

There are no salinity problems whatsoever in soil samples demonstrating slight alkaline reaction.

Soils with low lime level show a sandy loam texture. Available phosphorus in soils with low humus level and with medium total nitrogen level was found to be medium (0-30 cm) and low (30-60 cm), whereas available potassium was insufficient. In soils with sufficient (high) levels of available calcium and available magnesium, there are no problems with respect to available sodium. Available micronutrient elements in the soil samples including iron, copper and manganese were sufficient, whereas zinc was insufficient (Table1)

In the study, 4 kg/vines clinoptilolite that were taken from Gördes region of Turkey were applied to organic parcel and as a control weren't applied to organic parcel. Raisins produced from Sultani Çekirdeksiz grape variety in organic grape parcels during organic production phase (2006-2007).

Potassium (K), phosphorus (P), sodium (Na), iron (Fe), copper (Cu), zinc (Zn), manganese (Mn), calcium (Ca) and magnesium (Mg) contents of the raisin samples were determined in a series of analyses carried out using an ICP-AES spectroscopy during organic viticulture phase from 2006 to 2007.

The research was carried out as randomized block design trials with three replicates consisting of 12 vines per parcel. After a variance analysis was performed on the data obtained was using the statistical software package "SPSS 20.0 for Windows", an LSD (< 0.05) test was used for comparison of average values.

Mineral substance analyses were performed on raisin samples obtained from applications using an ICP-AES spectroscopy. A 10g raisin sample is placed in a crucible and dried in an incubator at 100 °C. The samples are then put into the oven when their temperature reaches 250 °C and the temperature is raised to 600 °C. They are left at this temperature overnight (13-15 hours). If the samples are not reduced to white ash, they are moistened with and dried in the oven for another 2 hours until they turn white. The crucibles are put in a desiccator and allowed to cool to room temperature. Later 6 ml extraction acid ($HCl+HNO_3$) and 50 ml distilled water are added to the crucibles and slightly heated to dissolve the ashes. The solution is strained into 100 ml volumetric flask using a black band filter and filled to the top with distilled water (The dilution factor should be 10.).

Desired standards were entered and the device is conditioned. Samples which had passed through the dilution procedure were fed into the device and Potassium (K), phosphorus (P), sodium (Na), iron (Fe), copper (Cu), zinc (Zn), manganese (Mn), calcium (Ca) and magnesium (Mg) minerals were read using the emission technique. The results obtained were multiplied by SF and mineral substance quantities were found.

Results and Discussion

Potassium (K), phosphorus (P), sodium (Na), iron (Fe), copper (Cu), zinc (Zn), manganese (Mn), calcium (Ca) and magnesium (Mg) contents of the raisin samples were determined in a series of analyses carried out using an ICP-AES spectroscopy organic parcel which were/weren't applied clinoptilolite from 2006 to 2007. Amounts of mineral substances found in raisin samples were given in ppm (parts per million). Mean values belonging to years of organic production were also given in ppm.

It was determined that trial applications conducted according to results of statistical evaluation of mean values of the control and applied clinoptilolite data for raisins obtained during the organic production phase over the years had different important effects on the potassium (K), calcium (Ca), magnesium (Mg) phosphorus (P), sodium (Na), iron (Fe), copper (Cu), manganese (Mn) and zinc (Zn) contents at 5 % significance level.

An increase was observed in mean values of potassium (K), calcium (Ca), magnesium (Mg) phosphorus (P), iron (Fe), manganese (Mn) and zinc (Zn) contents on applied clinoptilolite as compared to control. A decrease was observed in mean values of sodium (Na) and copper (Cu) contents on applied clinoptilolite parsel as compared to control.

As can be seen from Table 2, the highest Potassium (K) value was recorded at applied clinoptilolite, while the lowest value was observed control (7553.17 ppm and 7113.00 ppm, respectively). These results are similar to those reported by Yağcı and İlter (2007), Emine et al. (2011) and Gary and Arianna (2010) and Simsek et al. (2004) (7.47 mg/g) in seedless raisin. Potassium (K) is a very important component for human health. High-potassium diet lowers blood pressure and reduces cardiovascular disease morbidity and mortality (Whelton et al., 1997). In addition, potassium intake lowers urinary calcium excretion and decreases the risk of osteoporosis (He and MacGregor, 2008).

The highest calcium (Ca) value was recorded at applied clinoptilolite (237.83 and 284.46 ppm), while the lowest value was observed control (228,00 ppm) which can be seen in Table 2.

As can be seen from Table 2, the highest magnesium (Mg) value was recorded at applied clinoptilolite, while the lowest value was observed control (573.67 ppm and 488.67 ppm, respectively). These results are similar to those reported by Simsek et al. (2004) and Yağcı and İlter (2007). The Mg is essential to all living cells, where they play a major role in manipulating important biological polyphosphate compounds like ATP, DNA, and RNA. (He and MacGregor, 2008)

The highest phosphorus (P) value was recorded at applied clinoptilolite, while the lowest phosphorus (P) value was observed control (237.83 ppm and 215.33 ppm, respectively) which can be seen in Table 2. These results are similar to those reported by Simsek et al. (2004) and Yağcı and İlter (2007). Phosphorus can be found in the environment most commonly as phosphates. Phosphates are important substances in the human body, because they are a part of DNA materials and they take part in energy distribution (De Rosa et al., 1998).

As can be seen from Table 2, the highest sodium (Na) value was recorded control, while the lowest phosphorus (P) value was observed at applied clinoptilolite (167.33 ppm and 147.00 ppm, respectively) which can be seen in Table 2. These results are similar to those reported by Simsek et al. (2004) and Yağcı and İlter (2007).

The highest Iron (Fe) value was recorded at applied clinoptilolite, while the lowest value was observed control (20.77 ppm and 14.75 ppm, respectively) which can be seen in Table 2. These results are similar to those reported by Simsek et al. (2004), Yağcı and İlter (2007). Iron is an essential part of hemoglobin; the red colouring agent of the blood that transports oxygen through our bodies. Iron is needed for psychomotor development, maintenance of physical activity and work capacity, and resistance to infection (Stoltzfus, 2001).

An increase was observed in mean values of potassium (K), calcium (Ca), magnesium (Mg) phosphorus (P), iron (Fe), manganese (Mn) and zinc (Zn) contents on applied clinoptilolite as compared to control. A decrease was observed in mean values of sodium (Na) and copper (Cu) contents on applied clinoptilolite parsel as compared to control.

Our results prove that Organic raisins applied clinoptilolite constitute a natural source of energies and many minerals such as potassium (K), magnesium (Mg), copper (Cu), zinc (Zn), calcium (Ca), phosphorus (P) sodium (Na) iron (Fe) and manganese (Mn) that may prevent many diseases.

As can be seen from Table 2, the highest copper (Cu) value was control, while the lowest value was observed at applied clinoptilolite (6.35 ppm, ppm and 6.00 ppm, respectively).

The highest Manganese (Mn) value was recorded at applied clinoptilolite, while the lowest value was observed control (1.87 ppm and 1.55 ppm, respectively) which can be seen in Table 2. These results are similar to those reported by Simsek et al. (2004) and Yağcı and İlter (2007). Manganese is a constituent of metalloenzymes (arginase, pyrurate carboxylase and manganese superoxide dismutase) and an enzyme activator (hydrolases, kinases, decarboxylases and transferases). It is reguired for normal brain function (De Rosa et al., 1998)

As can be seen from Table 2, the highest zinc (Zn) value was recorded at applied clinoptilolite, while the lowest value was observed control (6.65 ppm and 6.43 ppm, respectively) which can be seen in Table 2. These results are similar to those reported by Simsek et al. (2004), Yağcı and İlter (2007). Zinc is needed for growth and for maintenance of immune function, which enhances both the prevention of and recovery from infectious diseases (Black,2003)

Abbreviations

Control: not applied clinoptilolite

C1: applied clinoptilolite
* Values in the same column with different subscript letters represent significant differences between production phases.
ns = not significant

Acknowledgements

This work was supported by the TAGEM [Grant number 111.05.2.001].

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Table 1. Physical analysis and Macronutrient and Micronutrient Contents of the Soil Sample

Soil Depth		**0-30 cm**	**30-60 cm**
pH		7,60	7,65
Soil salinity	(%)	0,025	0,025
Lime	(%)	3,44	3,92
Sandy	(%)	68,40	66,40
Silt	(%)	24,00	25,00
Clay	(%)	7,60	8,60
Texture		Sandy-loam	Sandy-loam
Organic Matter	(%)	1,52	0,95
Total Nitrogen	(%)	0,060	0,038
Available Phosphorus	(ppm)	3,32	1,29
Available Potassium	(ppm)	175	155
Available Calcium	(ppm)	2160	2400
Available Magnesium	(ppm)	934	938
Available Sodium	(ppm)	20,8	19,0
Available Iron	(ppm)	8,51	6,79
Available Copper	(ppm)	6,13	3,48
Available Zinc	(ppm)	0,67	0,52
Available Manganese	(ppm)	7,20	4,09

Table 2. Minerals content in Applied Clinoptilolite and Control of raisins produced from Sultani Çekirdeksiz grape variety during organic phase for Average of Years (2006-2007).

Aplication	**K*** **(ppm)**	**Ca*** **(ppm)**	**Mg*** **(ppm)**	**P*** **(ppm)**
Control	7113.00 b	228.00 b	488.67 b	215.33 b
C1	7553.17 a	237.83 a	573.67 a	237.83 a
LSD 0,05	170.65	6.13	44.63	15.70

Aplication	**Na*** **(ppm)**	**Fe*** **(ppm)**	**Cu*** **(ppm)**	**Mn** **(ppm)**	**Zn** **(ppm)**
Control	167.33 a	14.75 b	6.35 a	1.55 b	6.43 b
C1	147.00 b	20.77 a	6.00 b	1.87 a	6.65 a
LSD 0,05	18.15	4.81	0.18	0.21	0.15