

Elemental Composition of Red Wines in Southeast Turkey

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Abstract

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Mineral profiles of wines and soil extracts were analysed in the five most popular international wines (Cabernet Sauvignon, Syrah, Merlot, Cot, and Tannat) and national Boğazkere, which is one of the highest-quality grapevine varieties grown in Turkey. We carried out study to establish the mineral and metal concentrations in wines from Southeast Anatolia of Turkey. The ICP-OES method was used for accurate determination of concentrations of 12 elements including Ca, Cd, Co, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, and Zn. The high levels of iron, potassium, sodium, and calcium were observed in the wine samples analysed. Major elements were also abundantly found in the soil samples. Minor element contents of wine samples were compatible with results other researches. The amount of metal content in wine is an important issue. A remarkable finding of the study was that heavy metals like Pb (found below acceptable limits only in three samples), Co, and Cd were not detected. The results obtained did not exceed the maximum acceptable limits established by the Office International de la Vigne et du Vin. Our results showed that the mineral compositions of wine and soils were interrelated. The analysis of the soil samples taken from the vineyard locations showed similar results for highest composition of major minerals. The characteristics of the wines produced in the Southeast Region of Turkey were analysed for the first time.

Keywords: mineral content; *Vitis vinifera* L.; soil; ICP-OES

Turkey has strategic importance in the world since it is located at the intersection of the Mediterranean and Near Eastern gene centres. Anatolia, in particular, has been well-known for its grapevines throughout history, specifically in its Eastern and Southeastern regions that are commonly referred to as “the epicentre of viticulture and wine making” (AĞAOĞLU & ÇELİK 1987; AĞAOĞLU *et al.* 1998; ÇELİK *et al.* 1998). According to the reports published by major wine-producing countries, Turkey ranks the fifth in terms of the vineyard area (517 000 ha) and the sixth in terms of total grape production (4 275 659 t) among all the grape-growing countries (FAO 2012; OIV 2013).

Wine is composed of water, ethanol, saccharides, amino acids, phenolic compounds, and other pigments and trace metals (MONACI *et al.* 2003; ROIG & THOMAS 2003; KATALINIC *et al.* 2004; NILSSON *et al.* 2004). A number of factors affecting the mineral content of wines have been reported, including mineral composition of soil, viticultural practices,

environmental factors, fermentation process and the procedure of storage conditions (FERNANDEZ 1988; NÚÑEZ *et al.* 2000; MARINI *et al.* 2006). The metal content in wine is important due to their effect on the wine quality and on the health of consumers (NÚÑEZ *et al.* 2003; BANOVIC *et al.* 2009). Moreover, there are numerous factors influencing the metallic constituents of wine, such as specific production area, grape varieties, soil and climate, and wine-making process (NÚÑEZ *et al.* 2003). The situation highly depends on the capacity of vine to take up toxic elements, which are the consequence of pollution in the soil (VOLPE *et al.* 2009). The mineral content of wine is of great importance for characterising wine samples, identifying the wine origin, and assessing the nutritional safety of the product (ÁLVAREZ *et al.* 2007; GRINDLAY *et al.* 2008; GONZALVES *et al.* 2009; FABANI *et al.* 2010).

The mineral constituents of wine can be assessed by several analytical methods. However, most of the methods require extensive sample preparation. For

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this reason, using these methods takes a considerable amount of time and leads to relatively imperfect results. A fast and simple method for the quantification of the metal and mineral content of wine samples was determined by the inductively coupled plasma-optical emission spectrometry (ICP-OES) for using microwave digestion. In addition, a number of methods have been used for the assessment of metal concentration in wine, such as flame atomic absorption spectrometry (FAAS) (ONIANWA *et al.* 1999; ORTEGA-HERAS *et al.* 1999), electrothermal atomic absorption spectrometry (ETAAS) (FRESCHI *et al.* 2001; KARADJOVA *et al.* 2002), inductively coupled plasma mass spectrometry (ICP-MS) (MARENGO & ACETO 2003), and inductively coupled plasma optical emission spectrometry (ICP-OES) (WUILLOUD *et al.* 2001; AYDIN *et al.* 2009, 2010a).

Cabernet Sauvignon, Syrah, and Merlot are the most important varieties among red wines produced in the world. This study was carried out on the five most important international wine grape cultivars (Cabernet Sauvignon, Syrah, Merlot, Cot, and Tannat) and Boğazkere, one of the most important wine grape cultivars in Turkey. The aim of this study was to measure and analyse the mineral components in grape wines by using ICP-OES and comparison of trace element composition of vineyard soil samples. We applied ICP-OES to sequentially determine the 12 trace elements (Ca, Cd, Co, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Zn) in six red wine samples obtained from the Southeast region of Turkey.

MATERIAL AND METHODS

The trial site was located within a commercial vineyard in Diyarbakır. The red wines from the Southeast region of Turkey were collected during two vintage years (2011, 2012) in the Province of Diyarbakır (elevation: 677 m, 37°55.2'N, 40°13.8'E). This study was carried out on wines of the five most important international wine

grape cultivars (Cabernet Sauvignon, Syrah, Merlot, Cot, Tannat) and on one of the highest-quality Turkish red wine grape cultivar Boğazkere (Table 1). Three bottled wines were used for each cultivar and year. All analyses were replicated twice to obtain accurate results.

Standard solutions and reagents. An appropriate dilution of 1000 mg/l stock solution was used as the standard solutions for each metal (Merck, Darmstadt, Germany) immediately before usage. All the sampling and dilution steps were achieved using Milli-Q™ water (18.2 MΩ·cm) (Millipore Corporation, Bedford, USA). All the solutions were prepared in high-density polyethylene containers and were kept refrigerated. All the solvents and reagents were of analytical reagent grade.

Instrumentation. The assessments of 12 elements (calcium, cadmium, cobalt, copper, iron, potassium, magnesium, manganese, nickel, lead, sodium, and zinc) were done using a model Optima™ 2100 DV sequential inductively coupled plasma spectrometer (Perkin Elmer, Inc., Shelton, USA). The integration time used was 1.0 second. A microwave oven (Berghof Speedwave MWS-3; Berghof, Eningen, Germany) and specially made Teflon® vessels were used for the digestion procedure. The optimum instrumental conditions are given in Tables 2 and 3.

Samples and sample pretreatment. To analyse mineral composition and metal concentrations, an amount of 2.0 ml concentrated HNO₃ and 1.0 ml H₂O₂ was added into 5.0 ml of wine sample. The mixture was conveyed into a Teflon vessel, closed, and then put into the microwave oven. A 35-bar pressure was used in the oven and the digestion was performed in four steps, using a 10-min period for each step and temperature values of 100, 150, 160, and 100°C (AYDIN *et al.* 2010b). The entire procedure is summarised in Tables 2 and 3. The digested samples were transferred to 50 ml volumetric flasks, and deionised water was used to set the final volume. All of the elements were determined by ICP-OES. The blank digests were analysed using the same procedures.

Table 1. Wine samples

Sample No.	Producer/region	Grape variety	Wine types
1	Diyarbakır	Cabernet Sauvignon (international)	dry red
2	Diyarbakır	Syrah (international)	dry red
3	Diyarbakır	Merlot (international)	dry red
4	Diyarbakır	Cot (international)	dry red
5	Diyarbakır	Tannat (international)	dry red
6	Çermik/Diyarbakır	Boğazkere (national)	dry red

Table 2. Instrumental operating conditions for ICP-OES and HG-ICP-OES systems

Instrumentation	PerkinElmer Optima™ 2100 DV	
View	axial view	
Read	peak area	
Optical System	Echelle	
Power	1450 W	
Plasma Gas Flow	15 l/min	
Auxiliary Gas Flow	0.2 l/min	
Nebulizer gas flow rate	0.8 l/min	
Detector	Liquid state detector	
Sample Flow Rate	1.5 ml/min	
Nebulizer Nebulizing Chamber	Cyclonic	
Nebulizer	Concentric glass (Meinhard) type A	
Integration Time	1 s	
Source equilibration time	15 s	
Read delay	50 s	
Replicates	3	
Background correction	2-point (manual point correction)	
Spray chamber	Scot type spray chamber	
Nebulizer	Cross-Flow GemTip™ nebulizer (HF resistant)	
Purge gas	nitrogen	
Shear gas	air	
Plasma gas	argon	
Element	Wavelengths ICP-OES λ (nm)	LOD ($\mu\text{g/kg}$)
Ca	317.933	4.0
Cd	228.802	22.0
Co	228.616	15.0
Cu	327.393	4.0
Fe	238.204	7.0
K	766.490	100.0
Mg	285.213	35.0
Mn	257.610	25.0
Na	231.604	140.0
Ni	231.610	30.0
Pb	220.353	10.0
Zn	206.200	25.0

LOD – Limit of detection

Soil analyses

Samples and reagents. The soil at the trial site has a clayey texture. In terms of soil properties, the soil consists of 22% silt and 56.6% clay, 21.4% sand, 14% lime, and 1.8% organic material. Soil samples

Table 3. Instrumental operating parameters for microwave digestion procedure

Step	1	2	3	4
T ($^{\circ}\text{C}$)	100	150	160	100
T (min) ^a	10	10	5	5
Time (min) ^b	10	10	5	5

^alength of waiting time at the preferred temperature; ^btime between the two consecutive temperatures

were obtained from the lands where grape varieties were grown.

For this study, six soil samples (1 – Cabernet Sauvignon, 2 – Syrah, 3 – Merlot, 4 – Cot, 5 – Tannat, 6 – Boğazkere) were obtained from the Southeastern Anatolia in Diyarbakır, Turkey. In order to preserve the original quality of the soil, the samples were stored at ambient temperature in sealed plastic bags prior to any conditioning.

Nitric acid (HNO_3 65%), hydrochloric acid (HCl 36%), and hydrofluoric acid (HF 40%) were used for the digestion, all of which were of analytical grade (Merck, Darmstadt, Germany). Distilled water was used for every experiment following the additional purification with a Milli-Q™ system (Millipore Corporation, Billerica, USA). To ensure accuracy, all the analyses were repeated three times.

Digestion procedure for soil analysis. The digestion procedure for the soil analysis was performed using a Berghof MWS-3 model microwave digestion system (Berghof, Coral Springs, USA). The microwave acid digestion (MW-AD) procedure was performed as follows: after weighing 0.20 g of samples for each soil, the samples were conveyed into pressure-resistant PTFE vessels, followed by the addition of 4 ml of the acid mixture (HNO_3 -HCl-HF, 1 : 3 : 1).

The vessels were closed and heated in the microwave oven as shown in Table 5. The power applied was 600 W. For each metal, the limit of detection (LOD) was assessed as follows: 10 independent analyses of a blank solution spiked with the metal at a level of

Table 4. Temperature program of the microwave digestion system for soil samples

Step	1	2	3	4
T ($^{\circ}\text{C}$)	100	170	180	100
T (min) ^a	10	10	5	5
Time (min) ^b	10	10	5	5

^awaiting time at desired temperature; ^btime between the two sequential temperatures

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Table 5. Accuracy assessment through the analysis of the NIST 1643e trace elements in water

Element	Certified (mg/l)	Found (mg/l)	Recovery (%)
Cd	6.568 ± 0.073	6.484 ± 0.102	98.05
Ca	32 300 ± 1 100	32 985 ± 400	102.12
Co	27.06 ± 0.32	28.12 ± 0.14	103.92
Cu	22.76 ± 0.31	22.13 ± 0.17	97.23
Fe	95.7 ± 1.4	96.9 ± 0.4	101.25
K	2 034 ± 29	2 109 ± 8	103.69
Mg	8 037 ± 98	8 103 ± 21	100.82
Mn	38.97 ± 0.45	37.94 ± 0.11	97.36
Na	20 740 ± 260	20 231 ± 110	97.54
Ni	62.41 ± 0.69	61.47 ± 0.34	98.49
Pb	19.63 ± 0.21	19.14 ± 0.12	97.50
Zn	78.5 ± 2.2	77.7 ± 0.9	98.98

lower concentration of the analytical curve were carried out. The calculation of LOD was based on the standard deviation (δ) of these assessments ($\text{LOD} = 3 \times \delta$). The vessels were transported to another site and cautiously vented in a fume hood after cooling to room temperature in a water bath. To eliminate the acids after the digestion, an evaporation procedure was undertaken for the reaction mixture by using the evaporation module. Following the dissolution of residue in Milli-QTM water, the residue was filtered and the filtrate was diluted to a determined volume. Finally, the diluted solutions were measured for elements by using the ICP-OES analysis method.

Reference materials. The analytical results obtained by using the standard reference material (SRM)

are listed in Table 5. SRM 1643 E Trace elements in water obtained from National Institute of Standards and Technology (NIST, Gaithersburg, USA) was used.

RESULTS AND DISCUSSION

In this study, all the elements (Ca, Cd, Co, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Zn) were determined by ICP-OES. ICP-OES is an effective technique for trace element determination (AYDIN *et al.* 2010b, BAKIRDERE *et al.* 2011). The method proposed is simple and sensitive, allowing the adequate and simultaneous determination of Ca, Cd, Co, Cu, Fe, K, Mg, Mn, Na, Ni, Zn, and Pb by ICP-OES. The results of mineral composition measurements are summarised in Table 6. These results present mean values for the three measurements performed for each sample. The results of the analyses are summarised in Tables 6–8.

A high dispersion of the contents of the elements observed in wines was also described in the literature (NÚÑEZ *et al.* 2000; BANOVIĆ *et al.* 2009; ŞEN & TOKATLI 2014). Our results showed that the mineral compositions of wine and soils were interrelated. Table 8 shows the contents of the elements in the soils. The average contents of the elements in soil decrease in the following order: $\text{K} > \text{Na} > \text{Ca} > \text{Fe} > \text{Mg} > \text{Mn} > \text{Zn} > \text{Ni} > \text{Cu} > \text{Pb} > \text{Co} > \text{Cd}$. The soil contained essential major elements for grapevine growth. The constituents of major elements in soils are affected by the composition of the soil condi-

Table 6. Determination of macro elements found in wines by ICP-OES

Wine	Vintage	Ca	K	Na	Mg
Cabernet Sauvignon	2011	52.14 ± 6.23	387.01 ± 13.41	40.43 ± 2.05	27.22 ± 2.10
	2012	54.05 ± 3.14	354.27 ± 14.13	35.12 ± 2.46	29.41 ± 1.29
Syrah	2011	75.16 ± 6.34	682.45 ± 25.70	79.37 ± 4.28	53.32 ± 4.05
	2012	26.22 ± 1.01	207.34 ± 23.48	49.42 ± 3.23	38.16 ± 5.43
Merlot	2011	86.41 ± 4.27	312.39 ± 25.30	94.06 ± 8.27	45.24 ± 6.29
	2012	74.14 ± 8.24	289.11 ± 23.49	100.39 ± 9.25	51.31 ± 6.15
Tannat	2011	98.02 ± 9.31	302.37 ± 28.21	74.31 ± 9.11	68.03 ± 7.32
	2012	48.29 ± 2.14	265.02 ± 14.01	89.23 ± 5.29	26.11 ± 3.02
Cot	2011	61.32 ± 5.04	546.36 ± 28.15	49.22 ± 1.07	35.33 ± 1.07
	2012	64.27 ± 1.24	558.46 ± 10.20	53.09 ± 2.28	36.19 ± 3.31
Boğazkere	2011	67.23 ± 4.11	524.33 ± 32.16	52.47 ± 2.21	41.33 ± 4.28
	2012	65.37 ± 3.21	587.44 ± 16.52	54.23 ± 1.12	45.26 ± 2.17

All results are expressed in mg/l (mean ± SD); SD – standard deviation

Table 7. Determination of trace elements found in wines by ICP-OES

Wine	Vintage	Fe	Cu	Mn	Ni	Zn
Cabernet Sauvignon	2011	14.23 ± 3.15	0.43 ± 0.03	1.57 ± 0.38	0.46 ± 0.03	2.15 ± 0.75
	2012	13.35 ± 0.57	0.51 ± 0.02	1.41 ± 0.18	0.91 ± 0.09	2.09 ± 0.25
Syrah	2011	17.94 ± 1.15	0.97 ± 0.07	1.94 ± 0.08	0.95 ± 0.03	5.07 ± 0.85
	2012	14.21 ± 0.68	0.75 ± 0.05	1.01 ± 0.11	0.89 ± 0.05	1.58 ± 0.34
Merlot	2011	13.98 ± 1.59	0.88 ± 0.04	1.48 ± 0.14	0.52 ± 0.01	2.71 ± 0.45
	2012	13.58 ± 0.24	0.95 ± 0.06	1.57 ± 0.41	0.38 ± 0.03	2.56 ± 0.14
Tannat	2011	15.61 ± 0.29	0.93 ± 0.08	1.83 ± 0.27	1.18 ± 0.12	4.49 ± 0.13
	2012	15.08 ± 0.46	0.82 ± 0.09	1.87 ± 0.25	0.32 ± 0.05	4.89 ± 0.28
Cot	2011	9.14 ± 0.73	0.68 ± 0.07	1.27 ± 0.10	1.39 ± 0.34	4.05 ± 0.78
	2012	10.58 ± 0.32	0.82 ± 0.03	1.87 ± 0.41	1.46 ± 0.17	4.76 ± 0.24
Boğazkere	2011	29.64 ± 1.47	0.99 ± 0.04	1.61 ± 0.39	0.66 ± 0.03	1.62 ± 0.19
	2012	28.12 ± 1.34	0.98 ± 0.03	1.78 ± 0.45	0.68 ± 0.04	1.74 ± 0.83

All results are expressed in mg/l (mean ± SD); SD – standard deviation

tions. A similar trend was observed in some previous studies (NÚÑEZ *et al.* 2000; THIEL *et al.* 2004; BANOVIĆ *et al.* 2009).

Years did not have any effects on the macroelement levels of Cabernet Sauvignon, Cot, and Boğazkere but macroelement values changed by years in Syrah, Merlot, and Tannat wines.

According to the microelement values, no difference was found by the years for Cabernet Sauvignon, Merlot, Tannat, Cot, and Boğazkere wines but only trace elements changed for Syrah wines by years. These results can be attributed to soil and environmental conditions and cultural practices (irrigation, fertilisation etc.).

Based on the amount of concentration in wine, the elements were classified into two categories;

- (a) Fe, K, Na, Ca, and Mg were present in the highest concentrations;
- (b) Ni, Cu, Zn, and Mn were present in the lowest concentrations.

According to the results, Ca, Mg, K, Na and Fe elements were abundant both in the soil and wine samples. These major elements were also the most abundant elements found in wines, and thus they are the most frequently analysed elements (PÉREZ TRUJILLO *et al.* 2003).

Iron was detected in higher concentrations (9.14 to 28.12 mg/l). In general, Fe mineral was detected higher than 10 mg/l. A few mg/l of iron originating from the grapes (2–5 mg/l) is a major component of wines. The higher amount of Fe in soil is associated with the characteristics of the soil as well as the equipment and the stabilisation treatments (RIBÉREAU-GAYON *et al.* 2006). The highest Fe level was observed for the Boğazkere

grape cultivar, which originated from the Diyarbakır province of Southeast Anatolia. ALKİŞ *et al.* (2014) and ŞEN and TOKATLI (2014) studied similar wines (Boğazkere, Cabernet Sauvignon, Syrah, and Merlot) and their Fe content was lower than that in our results. The level of Fe in the Southeast region red wines was significantly higher than in Argentinian, Brazilian, and Spanish wines (LARA *et al.* 2005; SANTOS *et al.* 2010; RODRÍGUEZ *et al.* 2011). The Southeast Turkish soil features the terra rossa soil, which is known to be an iron-laden gritty soil. In our study, an excess of Fe in the wine may be associated with an excess of Fe in the soil (Tables 8 and 9).

Table 8. Determination of heavy elements found in wines by ICP-OES

Wine	Vintage	Co	Cd	Pb
Cabernet Sauvignon	2011	nd	nd	nd
	2012	nd	nd	nd
Syrah	2011	nd	nd	0.10 ± 0.01
	2012	nd	nd	0.10 ± 0.02
Merlot	2011	nd	nd	nd
	2012	nd	nd	nd
Tannat	2011	nd	nd	nd
	2012	nd	nd	0.11 ± 0.02
Cot	2011	nd	nd	nd
	2012	nd	nd	nd
Boğazkere	2011	nd	nd	nd
	2012	nd	nd	nd

All results are expressed in mg/l (mean ± SD); SD – standard deviation; nd – not detected

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Table 9. Determination of elements found in soil by ICP-OES

Soil sample	Ca	Cd	Co	Cu	Fe	K
1	94.01 ± 5.42	1.07 ± 0.01	0.80 ± 0.02	5.76 ± 0.41	95.25 ± 1.87	564.28 ± 33.41
2	98.36 ± 7.37	1.14 ± 0.19	0.94 ± 0.07	4.97 ± 0.56	123.14 ± 2.25	621.21 ± 15.30
3	125.38 ± 13.10	1.23 ± 0.12	0.98 ± 0.03	6.51 ± 0.95	108.35 ± 2.48	589.23 ± 13.12
4	104.41 ± 10.28	0.78 ± 0.01	nd	5.89 ± 0.91	98.75 ± 3.61	635.37 ± 12.30
5	129.08 ± 19.33	1.85 ± 0.18	nd	8.35 ± 0.59	150.42 ± 3.47	701.28 ± 34.44
6	122.17 ± 8.48	0.67 ± 0.09	nd	11.36 ± 0.74	148.35 ± 4.27	578.03 ± 10.28
	Mn	Mg	Na	Ni	Pb	Zn
1	12.54 ± 0.92	58.11 ± 2.05	101.07 ± 6.33	1.48 ± 0.12	1.25 ± 0.09	11.94 ± 1.13
2	11.23 ± 0.56	65.28 ± 2.34	124.48 ± 14.15	1.79 ± 0.37	1.94 ± 0.23	12.18 ± 0.93
3	11.39 ± 0.84	39.21 ± 3.40	105.21 ± 9.38	1.98 ± 0.14	1.32 ± 0.28	12.87 ± 1.38
4	10.05 ± 0.23	47.38 ± 6.31	110.16 ± 11.37	1.57 ± 0.23	1.29 ± 0.08	11.32 ± 1.57
5	15.25 ± 0.37	63.11 ± 2.18	142.23 ± 31.17	1.04 ± 0.20	1.43 ± 0.32	14.35 ± 1.02
6	12.89 ± 0.74	71.27 ± 5.14	153.34 ± 16.42	1.69 ± 0.17	1.35 ± 0.25	15.14 ± 0.97

All results are expressed in mg/kg (mean ± SD); SD – standard deviation

Potassium exhibits higher concentrations than the rest of the elements. In our samples, the highest level of K (682 mg/l) was detected in the Syrah red wine (vintage year 2011) (Table 5). Potassium is the main positive ion in wine (BOULTON *et al.* 1996). A number of factors affect the amount of potassium in wine, including the variety of grapes, soil and climatic conditions, time of harvest, the temperature of fermentation and storage, and the pH and the use of ion-exchange resins (NÚÑEZ *et al.* 2000). Its concentration in wine ranges from 200 mg/l to 2000 mg/l (MARGALIT 1997). The high level of potassium in wine has great nutritional values. SANTOS *et al.* (2010) found a higher (1032 mg/l) level of K in Cabernet Sauvignon Brazilian wines. The K levels in Turkish wines were lower than the levels in Brazilian, Californian, and Spanish wines (OUGH *et al.* 1982; SANTOS *et al.* 2010; RODRÍGUEZ *et al.* 2011) but consistent with Chinese wines (DU *et al.* 2012).

Sodium was detected between 35 and 100 mg/l. Sodium is the main extracellular cation. It participates in the maintenance of the acid-base balance and in osmotic regulation. The Na mineral level is extremely higher than in other studies (KMENT *et al.* 2005; RODRÍGUEZ *et al.* 2011). This principal component can be related to soil composition and winemaking process (NÚÑEZ *et al.* 2000). Excessive Na content in soil causes the salinity problem, which is a very important matter in the Southeastern region of Turkey, an area which has insufficient rain and corresponding high evaporation (KENDIRLI *et al.* 2005). The high content

of Na in wines (35–100 mg/l) can be attributed to the high content of Na in soil (101–142 mg/kg) (Table 8).

Calcium is a natural component of berries. In our study, the Ca mineral content ranged between 26 and 75 mg/l in all wine samples. The Ca concentration of Merlot wine was found to be 74–86 mg/l. However, 48.61–59.12 mg/l were found in Southern Brazilian Merlot wines (DUTRA *et al.* 2010). The concentration levels of Ca in our study were close to the values found in other researches (OUGH *et al.* 1982; ANJOS *et al.* 2003; ÁLVAREZ *et al.* 2007; RODRÍGUEZ *et al.* 2011; DU *et al.* 2012; ŞEN & TOKATLI 2014). Since the mean calcium content in wine is 80 mg/l, it can result in tartrate instability in wine. However, calcium leads to no problems under normal circumstances, and the fining process can be a pathway for calcium entry in wine (bentonite, DE, filter pads) (MARGALIT 1997).

Magnesium content in wines correlates with the natural Mg content of grape berries. Mg concentration ranged from 26 mg/l to 68 mg/l (Table 6). Mg level was measured to be 27–29 mg/l in the Cabernet Sauvignon grape cultivar. In our study, the Mg level in the Cabernet Sauvignon wine samples was lower than in Cabernet Sauvignon (80.30–98.52 mg/l) and Merlot (79–90 mg/l) wines produced in Southern Brazil (DUTRA *et al.* 2010) and Cabernet Sauvignon (80–160 mg/l) wines produced in China (DU *et al.* 2012). The Mg content in wines can be attributed to a number of factors including the soil composition, pH, the time, the temperature of storage, and the rate of pressing (ORTEGA-HERAS *et al.* 1999; FRÍAS *et al.* 2003).

The manganese concentration ranged from 1.01 mg/l to 1.94 mg/l (Table 7). Mg and Mn, which are mobile elements in soils, are major micronutrients for plants and grape berries (MARENGO *et al.* 2003; THIEL *et al.* 2004; RODRÍGUEZ *et al.* 2011). The Mn levels in Cabernet Sauvignon and Merlot wines produced in Southern Brazil were consistent with the levels in our study. Nickel concentration ranged from 0.32 mg/l to 1.39 mg/l (Table 7), and copper concentration ranged from 0.51 mg/l to 0.99 mg/l (Table 7). The Mn and Ni contents in the wine samples were compatible with the other research results (DUTRA *et al.* 2010; SANTOS *et al.* 2010; DU *et al.* 2012; ALKIŞ *et al.* 2014; ŞEN & TOKATLI 2014).

Zinc, which is a trace element naturally found in soil, plays a key role in the growth of plants. Zinc content was detected between 1.58 and 4.89 mg/l (Table 7). In all wines, the zinc content was lower than the allowable level (5 mg/l), which was established by the Office International de la Vigne et du Vin (OIV 2013). Higher concentrations may result from vineyard, equipment or prolonged maceration and may lead to unfavourable effects on the sensory properties of wine (IBANEZ *et al.* 2008; OIV 2013).

The copper concentration of analysed wine samples was found lower than the maximum acceptable limit. The maximum acceptable limit of Cu mineral content is established as 1 mg/l by the Office International de la Vigne et du Vin (OIV 2013). The Cu concentration levels detected in our study were close to the values found by ŞEN and TOKATLI (2014) in similar wines. The low content of Cu in wines may be a result of surface contamination caused by the pesticides that involve copper sulphate, such as Bordeaux mixture (Cu SO₄) (SANTOS *et al.* 2010).

An important finding of the study was that heavy metals like Co, Cd, and Pb (except for only three samples below acceptable limits) were not detected in our samples. The quantity of metal concentrations in wine is a major issue since they affect the quality of the wine and hygienic properties and they have toxicological effects on health (FERNANDEZ 1988). Some of the metals take part in a fermentation process, whereas small concentrations of some metals are critically necessary for the development of plants and animals, because higher concentrations exacerbate the toxic effects (RIBÉREAU-GAYON *et al.* 2006). Only three samples (Syrah 2011–2012) of all analysed wine samples contained lower levels of Pb than the upper limit of 0.15 mg/l established by the Office International de la Vigne et du Vin (OIV

2013). Nevertheless, ŞEN and TOKATLI (2014), had been found the western wines, where industrialisation is high discriminated themselves with relatively higher amounts of Pb, but still less than the allowable maximum level. If the quantity of heavy metals is higher than the allowed limits, the wine producers should be more cautious about the content of heavy metal in their wines. The heavy metals cobalt and cadmium were not detected in any of our wine samples (Table 8).

CONCLUSION

In this work the mineral composition of bottled international popular red wines (Cabernet Sauvignon, Syrah, Merlot, Cot, and Tannat) and national popular red wine Boğazkere produced in the Southeast region of Turkey was studied in order to analyse the mineral composition of wine samples and the mineral composition of vineyard soil samples was also analysed. The ICP-OES ensures very good detection and offers the right conditions for a reliable and fast determining method. We used the ICP-OES method successfully in our study. The high level of iron, potassium, sodium, and calcium was observed in analysed wine samples. Major elements in the soil can be associated with the soil structure. Soil samples taken from vineyard locations showed similar results for the highest major mineral composition. An important finding of the study was that the heavy metals Co, Cd, and Pb were not detected (except for only three samples below acceptable limits). This situation can be explained by the limited industrialisation of the Southeast region of Turkey. Therefore, we can say that the soil contamination has not occurred in the area yet. The level of the metal content in wine is a major issue because of its toxic effects on health. Principal elements like K, Ca, and Na were abundant in our wine samples like in other studies. These elements are also important for the geographical classification of wines. We conclude by saying that the discrimination of mineral content of Southeast Anatolian wines presented by this study can be used to obtain a successful regional classification for future studies.

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