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RESEARCH PAPER

Multi-element analysis and differentiation of Chilean wines using mineral composition and multivariate statistics

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Abstract

Y. Mirabal-Gallardo, M. A. Caroca-Herrera, L. Muñoz, M. Meneses, and V. F. Laurie. Multi-element analysis and differentiation of Chilean wines using mineral composition and multivariate statistics. 2018. *Cien. Inv. Agr.* 45(2): 181-191. The concentration of seventeen metal elements was analyzed in 130 commercial samples of Chilean wines, using flame atomic absorption spectroscopy (AAS) and inductively coupled plasma–mass spectrometry (ICP-MS). The elements analyzed were within the usual concentration ranges previously reported in other wine regions (for example: Fe, 2.08 ± 0.99 mg L⁻¹; Zn, 0.71 ± 0.44 mg L⁻¹; K, 788 ± 219 mg L⁻¹; and Na, 14.62 ± 8.6 mg L⁻¹). When the metal content of the samples was compared among geographic areas, significant differences in the concentration of K, Na, Mn, Mg, Zn, and Cr were observed ($p \leq 0.05$). Moreover, principal component and linear discriminant analyses, used to discriminate wines according to geographic area, obtained adjustments above 90% for white wines and over 70% for red wines.

Keywords: AAS, classification, element, ICP-MS, metal, multivariate statistics, wine.

Introduction

Mineral elements have an important influence on the quality of grapes and wines. Some of these elements are essential for the proper metabolic function of vines and should be added as nutrients if their natural concentration is limited (Iland and

Coombe, 1988). In musts and wines, the composition of metals influences the pH, ion balance, yeast activity, color, and the chemical and oxidative stability of the product (Pohl, 2007; Tariba, 2011).

The analysis of these constituents is used to assess the presence of contaminants, verify their concentration for winemaking purposes (e.g., metal haze formation), and to ensure that the regulatory requirements for commercialization are met. Similarly, this information has been

used to verify the wine's authenticity based on the correlation between metal composition and geographic origin (Arvanitoyannis *et al.*, 1999; Zou *et al.*, 2012; Versari *et al.*, 2014).

To date, a number of studies have analyzed wine provenance based on metal composition (Castiñeira *et al.*, 2004; Coetzee and Vanhaecke, 2005; Angus *et al.*, 2006; Zou *et al.*, 2012; Aceto *et al.*, 2013; Alkis *et al.*, 2014). In some of these studies, the authors have found a good correlation between the content of metals in the soil, grapes and wine (Coetzee *et al.*, 2005; Pohl, 2007; Zou *et al.*, 2012), allowing for a good degree of sample differentiation when a large number of metal elements and wine samples were analyzed (Coetzee *et al.*, 2014; Paneque *et al.*, 2017). However, other reports have revealed that certain viticulture and winemaking practices may alter the content of metals (e.g., vineyard fertilizers, plant protection products, winemaking aids such as bentonite, etc.), thus limiting the ability to find correlations between the mineral content of the soils and those of finished wines (Almeida and Vasconcelos, 2003; Catarino *et al.*, 2007; Aceto *et al.*, 2013; Hopfer *et al.*, 2015).

In the case of Chilean wines, only one attempt has been made to characterize the content of metals (Laurie *et al.*, 2010). In that study, seventy-five wine samples were analyzed for K, Mg, Ca, Na, Fe and Zn, with most of them being within the usual concentration ranges previously reported for other wine regions. Additionally, it was observed that wines produced near coastal areas had a much higher content of Na than those produced in other viticultural areas. Aside from that study, we are not aware of any attempts to characterize the composition of a wider range of elements or to differentiate Chilean wines according to their metal composition. Therefore, the aims of this work were to study the concentration of seventeen macro and microelements in Chilean wines and to use multivariate statistics to identify discriminating elements that could allow for us to group samples according to geographic origin.

Materials and Methods

Wine samples

The study included 130 bottles of commercial wines representing six varieties, two viticultural regions, six subregions, four zones/areas (Figure 1), and three different vintages (Table 1). These samples were donated by different wineries or purchased from local stores and were selected based on a similar price range (approximately US\$ 5 to 10). The alcohol strength of the samples varied between 12.5 and 14% for white wines and 13 to 14.5% v/v for reds. Their pH ranged from 2.99 to 3.44 for white wines and 3.04 to 3.68 for reds (Table a, supplemental information).

Reagents and solutions

All solutions were prepared using ultra-pure water, obtained from a Millipore system (Bedford, MA, USA). Nitric acid (HNO₃, 65%) and hydrogen peroxide (H₂O₂, 30%) were purchased from Sigma Aldrich (Darmstadt, Germany), and Lanthanum oxide (La₂O₃) was bought from Merck (Darmstadt, Germany). The calibration curves for K, Na, Mg, Ca, Fe, Zn, Cu and Mn were prepared from certified individual commercial solutions of 1000 mg L⁻¹ as explained below (Spex Industries Inc., Edison, NJ, USA). Additionally, a Certipur® ICP multi-element standard solution of 1000 mg L⁻¹ obtained from Merck was used to develop the calibration curves for the analyses of microelements.

Glassware was cleaned by soaking in 10% v/v HNO₃ solution for 24 h and rinsed at least three times with ultra-pure water. Then, the material was dried and stored in a class-100 laminar flow hood.

Calibration curves

Five-point calibration curves were prepared for each of the seventeen metals studied (i.e., K, Na,

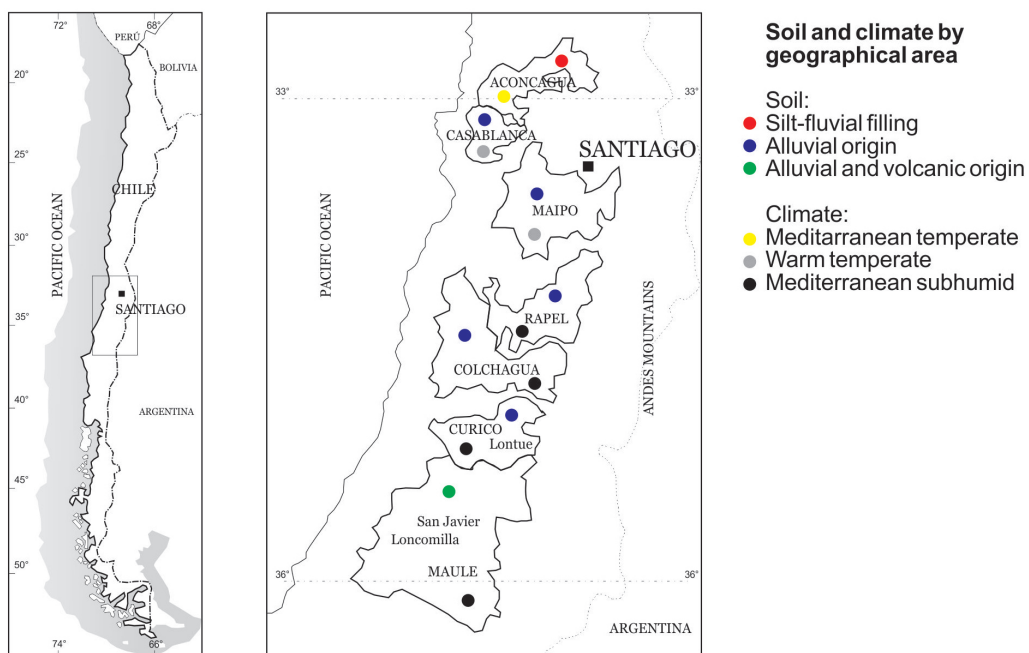


Figure 1. Wine regions of Chile.

Table 1. Wine samples used for the analysis of mineral composition.

Wine type	Viticultural Region	Subregion	Zone/area	Number of samples and varieties	Vintages
White (n=39)	Aconcagua	Aconcagua	-	2 Ch, 2 Sb	2013
		Casablanca	-	3 Ch, 2 Sb	2011-2013
	Central Valley	-	-	5 Ch, 4 Sb	2011-2013
		Rapel	Colchagua	1 Sb, 2 Vi	2013
		Curicó	-	1 Ch, 3 Sb	2012-2013
			Lontué	1 Ch, 1 Sb	2012-2013
		Maule	-	2 Ch, 7 Sb	2012-2013
	Loncomilla/ San Javier	2 Ch, 1 Sb	2013		
Red (n=91)	Aconcagua	Aconcagua	-	1 CS, 1 Cr, 1 Me, 1 Sy	2012
	Central Valley	-	-	8 CS, 3 Cr, 7 Me, 1 Ma, 1 Pn, 1 Cf	2011-2013
		Maipo	-	3 CS, 1 Cr	2011-2013
		Rapel	-	3 CS, 3 Me	2011-2013
			Colchagua	3 CS, 6 Cr, 2 Me, 3 Sy	2011-2013
		Curicó	-	5 CS, 3 Me, 1 Sy, 1 Cf	2010-2013
			Lontué	1 CS, 2 Cr, 1 Sy, 1 Cf	2010-2012
		Maule	-	5 CS, 7 Cr, 4 Me, 2 Sy, 3 Ma, 2 Pn	2011-2013
			Loncomilla/ San Javier	1 CS, 1 Me/ 1 CS, 1 Cr, 1 Sy	2012

Where: Ch, Chardonnay; Sb, Sauvignon blanc; Vi, Viognier; CS, Cabernet Sauvignon; Cr, Carmenère; Me, Merlot; Sy, Syrah; Ma, Malbec; Cf, Cabernet franc; Pn, Pinot noir.

Ca, Zn, Cu, Fe, Mg, Mn, Ni, Cr, Al, Pb, Cd, Hg, Se, Co and Sn). For the atomic absorption spectroscopy (AAS) analyses, they were prepared from certified standard solutions of 1000 mg L⁻¹ of each metal. The concentration ranges covered for each calibration curve were as follows: Ca, 1-25 mg L⁻¹; Mg, 0.25-5 mg L⁻¹; K, 2-20 mg L⁻¹; Na, 1-10 mg L⁻¹; Mn, 1-6 mg L⁻¹; Cu, 0.5-5 mg L⁻¹; Fe, 1-10 mg L⁻¹, and Zn, 0.5-3 mg L⁻¹. Before measuring the macroelements (Ca, Mg, K and Na) in the AAS, a 1:10 v/v dilution of the samples was performed with La₂O₃ (1.1 g L⁻¹ solution). Conversely, Mn, Cu, Fe and Zn were determined with no dilution because of their low concentration.

The inductively coupled plasma-mass spectrometry (ICP-MS) analyses were based on the methodology reported by Aceto and collaborators (Aceto *et al.* 2013). The certified standard solution was a mixture of 5% HNO₃ solution (w/v) with the following additions: 10.0 mg L⁻¹ for Ca, Cd, Cr, Fe, Na, Ni, Pb, Se, and Zn; 10.1 mg L⁻¹ for Al, Co, Cu, Mn, Rb, and Sr; and 9.9 mg L⁻¹ for Hg, K, and Mg. From this solution, a calibration curve was prepared with the following concentration points: 0.0002, 0.0005, 0.001, 0.003, 0.007, 0.01, 0.03, 0.05, 0.07, and 0.1 mg L⁻¹, using nitric acid (Suprapur®) for dilution (5% w/v). The calibration curves obtained had coefficients of determination, R², ranging between 0.997 and 0.999.

Wine analyses

Once opened, the wine from each bottle was subjected to microwave-assisted acid digestion in order to eliminate organic interfering compounds (Alkis, *et al.*, 2014; Grindlay, *et al.*, 2009). Five mL of wine, 3 mL of 65% HNO₃ and 1.5 mL of H₂O₂ 30% were placed in 55 mL Teflon® tubes (MARS Xpress, Matthews, NC, USA). The samples were manually shaken for approximately 10 seconds and left to rest for 24 h before proceeding with the microwave-assisted heating program, which included a ramp time of 5 minutes going from 20 to 175 °C with a 3 min hold time, followed by a 5 min ramp from 175 to 30 °C with a hold time

of 3 min. This cycle was repeated twice at 800 W of applied power.

Once the samples were digested, the content of each Teflon tube was transferred into a 50 mL volumetric flask and filled with ultra-pure water before the analyses in the AAS or ICP-MS were performed.

The analysis for the most concentrated elements (i.e., Ca, K, Na, Mg, Cu, Mn, Fe and Zn) was completed in an AAS (280FS AA, Agilent Technologies), whereas trace metal ions (i.e., Al, Cd, Cr, Hg, Ni, Pb, Se, Sn and Co) were analyzed with an ICP-MS (7700x, Agilent Technologies), using argon gas to form the plasma for the instrument. The ICP-MS was equipped with an ASX 500-CETAC auto-sampler, a micro-concentric nebulizer, nickel cones, and a peristaltic sample delivery pump. The operation conditions of the AAS and ICP-MS are detailed in Table 2.

Table 2. Instrumental conditions for atomic absorption spectroscopy (AAS) and inductively coupled plasma-mass spectrometry (ICP-MS) analyses.

Parameters	Value
AAS	
Flame	Air/acetylene
Air flow (L min ⁻¹)	13.50
Flow acetylene (L min ⁻¹)	2.00
Burner height (mm)	13.5
Slit width (nm)	0.2-1.0
Lamp current (mA)	4-10
Metals	Wavelength (nm)
K	766.5
Na	589.0
Ca	422.7
Mg	285.2
Cu	324.8
Zn	213.9
Fe	248.3
Mn	279.5
ICP-MS	
RF generator frequency (MHz)	27
RF applied power (W)	1550
Plasma gas flow rate (L min ⁻¹)	15
Auxiliary gas flow rate (L min ⁻¹)	0.9
Nebulizer gas flow rate (L min ⁻¹)	1.03
Stabilization delay (s)	10
Internal standards	Sc and Er
Number of masses	32

Each wine bottle was sampled, pre-treated, and analyzed three times. Each of the analytical readings was also repeated three times.

Data analysis

The metal content of the samples was analyzed using descriptive statistics (i.e., mean, range, standard deviation, and median) and presented as the average of all the wine samples, or separated into white and red wine subgroups.

One-way analysis of variance (ANOVA), followed by a post hoc Tukey test, was conducted for each element, looking for metals that could allow for the grouping of samples according to their place of origin ($p \leq 0.05$). Additionally, principal component analysis (PCA) was used to identify the main elements that explain the data variance, whereas linear discriminant analysis (LDA) was used for sample discrimination (Angus *et al.* 2006; Laurie *et al.*, 2010; Coetzee *et al.* 2014). These latter analyses (i.e., PCA and LDA) were performed separately for white and red wines, excluding the samples representing the Central Valley ($n=30$ white and 70 red wine samples). These analyses were done at a subregional level to avoid collinearity between samples of different hierarchical classification.

To avoid attributing subregional differences to wines whose metal profiles could have been influenced by varietal disparities, multivariate analyses were conducted only with metals that did not show significant differences according to varieties (e.g., Zn, Ca, Na, Mn, Fe, Cu, K, Al, Sn, Pb, Ni, and Cr in white wine and Zn, Ca, Na, Mn, Mg, Fe, Cu, K, Al, Sn, Ni, and Cr in red wine) (Table b, supplemental information).

In all cases, the statistical analyses were performed using Statgraphics Centurion XV (Statpoint technologies, Warrenton, VA, USA), and graphical representations were made using Sigma-Plot version 12 (Systat Software Inc. Chicago, IL, USA).

Results and Discussion

Table 3 shows a summary of the identified concentrations of the main metal elements. As expected, K was the metal with the highest average concentration, followed by Mg, Ca and Na. The least prevalent metal elements, with concentrations below 0.001 mg L⁻¹, were Cd, Hg, Co, Se, and Pb (data not included). These results agree with previously published data for other wines and regions, from which the following concentration ranges have been reported: K, 125 - 2040 mg L⁻¹; Ca, 50 - 300 mg L⁻¹; Na, 3 - 279 mg L⁻¹; Mg, 32 - 245 mg L⁻¹; Fe, 0.6 - 16.1 mg L⁻¹; Zn, 0.07 - 5.6 mg L⁻¹; Mn, 2.4 - 7.5 mg L⁻¹; Cd, 0.00 - 0.03 mg L⁻¹; Cu, 0.02 - 2.41 mg L⁻¹; Pb, 0.001 - 0.62 mg L⁻¹; Co, 0.004 - 0.04 mg L⁻¹; Cr, 0.002 - 0.23 mg L⁻¹; Ni, 0.00 - 0.13 mg L⁻¹; Sn, n.d - 0.003 mg L⁻¹; Se, 0.0003 - 0.004 mg L⁻¹, etc. (Ough *et al.*, 1982; Iglesias *et al.*, 2007; Pohl, 2007; Hopfer *et al.*, 2015).

Red wines have statistically higher concentrations of K, Mg, Mn, Fe, and Cr when compared with white wines, where Ca and Na were more prevalent. The former is mainly explained by winemaking differences such as skin extraction during red wine fermentation (Serapinas *et al.*, 2008; Vázquez *et al.*, 2013). For example, K is highly concentrated in the pericarp of the fruit, and long maceration periods, such as those occurring during red wine fermentation, result in an increased concentration of this metal element (Storey, 1987; Iland and Coombe, 1988). On the other hand, an elevated concentration of Na in white wines has been attributed to the edaphoclimatic characteristics of certain areas in which these wines are produced, such as a limited rainfall and accumulation of this element in the soil (González *et al.*, 1996; Laurie *et al.*, 2010).

Content of metals and wine discrimination according to geographic area

Statistical differences were observed for several of the metals analyzed ($p \leq 0.05$) when the samples

Table 3. Summary of the concentration of metallic elements for the selected Chilean wine samples.

	Ion concentration (mg L ⁻¹)												
	Ca	Mg	K	Na	Mn	Cu	Zn	Fe	Al	Cr	Ni	Pb	Sn
All wines (<i>n</i> = 130)													
Mean	52	92	788	15	1.4	0.4	0.7	2.08	1.2	0.013	0.007	0.03	0.03
SD	12	18	220	9	0.6	0.3	0.4	0.99	0.9	0.008	0.005	0.02	0.02
Range	29-97	38-145	254-1251	3-65	0.01-3.1	0.005-1.3	0.01-4.1	0.19-5.89	0.008-6.5	0.003-0.07	0.001-0.03	0.003-0.86	0.01-0.32
Median	51	92	817	12	1.4	0.3	0.7	1.94	0.95	0.01	0.01	0.01	0.01
White wines (<i>n</i> = 39)													
Mean	56	78	530	22	1.2	0.4	0.8	1.2	1.2	0.013	0.005	0.03	0.03
SD	13	18	127	10	0.5	0.3	0.6	0.6	0.7	0.004	0.004	0.02	0.02
Range	33-94	38-116	254-749	5-65	0.01-1.96	0.1-1	0.01-4.1	0.19-2.8	0.007- 3.6	0.003-0.03	0.001-0.02	0.003-0.25	0.01-0.28
Median	55	80	549	20	1.3	0.4	0.7	1.2	1.2	0.01	0.01	0.02	0.01
Red wines (<i>n</i> = 91)													
Mean	50	98	899	11	1.5	0.4	0.7	2.4	1.2	0.021	0.007	0.04	0.03
SD	11	14	145	6	0.6	0.3	0.3	0.9	1.00	0.006	0.006	0.03	0.02
Range	29-97	65-145	515-1276	3-42	0.37-3.1	0.005-1.3	0.18-1.4	0.88-5	0.008-6.5	0.003-0.07	0.001-0.03	0.003-0.86	0.01-0.32
Median	49	96	910	10	1.5	0.3	0.6	2.4	0.9	0.01	0.01	0.01	0.01

were grouped and compared based on the location declared on their labels. For example, Maipo wines (predominantly producing Cabernet Sauvignon) had a higher concentration of K when compared with Aconcagua, Casablanca (predominantly producing white wines), and Curicó valleys. Colchagua and Maipo wines had more Mn than Curicó samples. Casablanca wines had more Na than most of the other wines. Colchagua wines had more Zn than Lontué and Loncomilla samples. Metal elements such as Ca, Cu, Fe, Al, Ni, Sn and Pb did not show significant differences among the wines compared from different geographic areas (Figure a, supplemental information).

Geological and climatic differences seemed to be decisive in the concentration of some of these elements (Zou *et al.*, 2012; Coetzee *et al.*, 2014; Paneque *et al.*, 2017). For example, a high Na content in Casablanca could be due to the presence of saline ground water or sea winds that contain salty water could reach some of these vineyards (Pohl, 2007; Blume *et al.*, 2015). This could be exacerbated by the limited rainfall experienced in recent years; this is similar to semi-arid areas where these types of cations accumulate in the

soil due to the scarcity of rainfall (González *et al.*, 1996; Sierra *et al.*, 2001).

Principal component analysis

Given the differences observed in the concentration of metals among the geographic areas studied, PCA was performed to identify the main vectors that explain the variability for these samples. An initial multivariate analysis was carried out for data reduction, allowing for the removal of elements that had strong linear correlations (Hopfer *et al.*, 2015). Metal elements that showed significant differences in their concentration between white and red varieties were also excluded from the multivariate analyses (Mg in case of white varieties, and Pb in case of red varieties), thus limiting the influence of varietal differences on the geographic area discrimination.

When a PCA was performed comparing red and white wines, 84.50% of the variability was explained by the first two principal components. In this case, the variability was mainly explained by the content of Na and the concentration of

Mg and K (Figure 2a). Consequently, further analyses were performed separately for white and red wines; values for the first two principal components reached 95.28% for white wines and 77.69% for reds (Figure 2b and c). The main components that explained the variability among groups of samples were clearly identified in white wines but not as much in reds, where a higher degree of overlapping among neighboring subregions and zones (and even areas) was observed (e.g., Rapel, Maule, San Javier, Loncomilla). This finding was probably because Maule is the largest viticultural area in Chile (Figure 1) with

approximately 30,296.1 Km² that spans from the coast to the Andes (ODEPA 2016).

Linear Discriminant Analysis

Given the results obtained by PCA, linear discriminant analysis (LDA) was used to divide the sample space, to separate the best possible subgroups, and to discriminate wines according to geographic area. As before, red and white samples were treated separately.

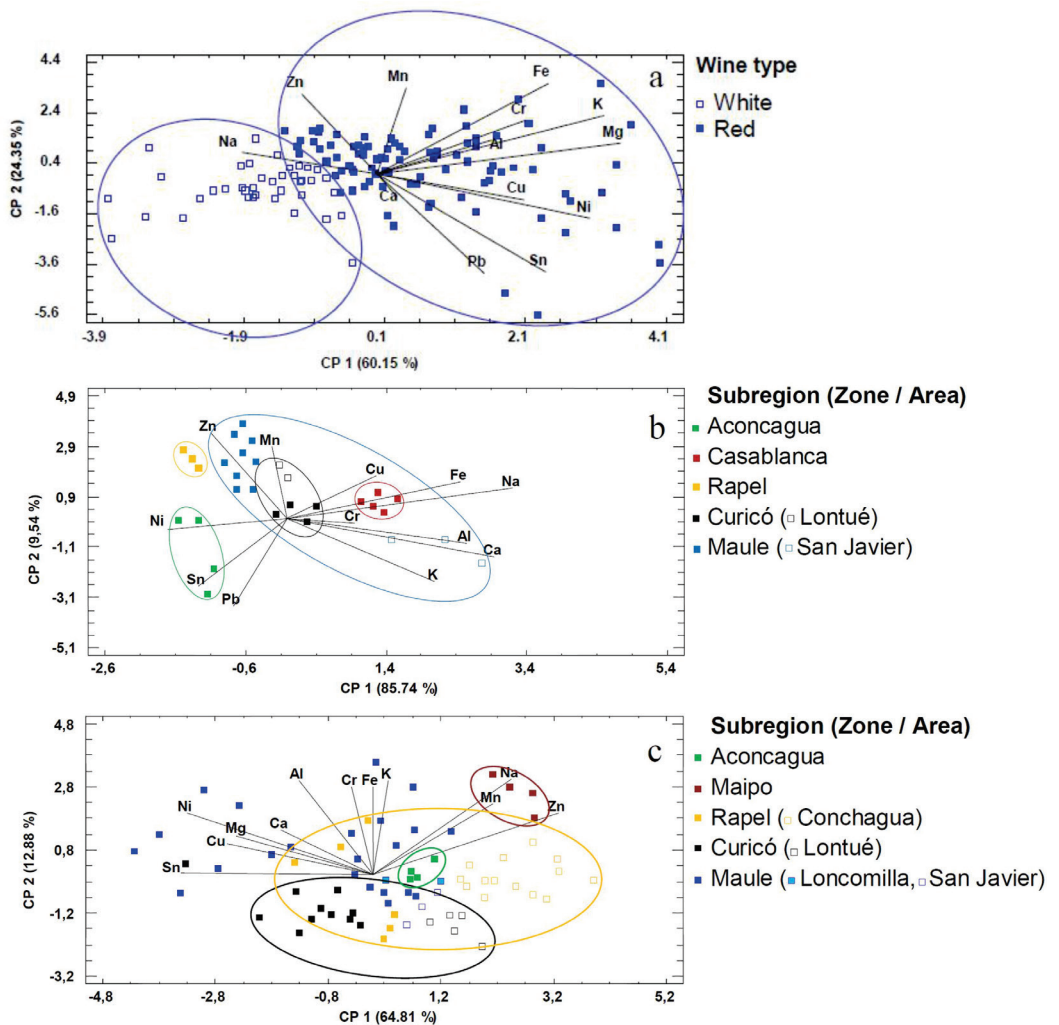


Figure 2. Score plot of the first two principal components (principal component analysis, PCA) of (a) 130 Chilean wine samples grouped by the type of wine, (b) 39 white wines grouped by geographic origin, and (c) 91 red wines grouped by geographic origin.

In the case of white wines, the magnitudes of twelve independent variables (i.e., Ca, K, Cu, Na, Mn, Fe, Zn, Al, Cr, Ni, Sn and Pb) were used as predictors to discriminate thirty wine samples according to their places of origin. The model allowed for a 96.9% discrimination of white wines according to their places of origin (Figure 3a). As shown in Figure 3a, the samples representing the five subregions studied were well grouped. As indicated before, the wines labeled under the Central Valley denomination were eliminated from these analyses because they include wines containing grapes may have come from different geographic origins. A minimum of 75% of the grapes should come from a specific region to label a wine from a specific place in Chile (Ministerio de Agricultura, 1995).

In the case of red wines, twelve predictor variables (Ca, K, Cu, Na, Mn, Fe, Zn, Al, Cr, Ni, Sn and Mg) were used to discriminate seventy samples according to their place of origin. In this case, the model allowed for 79.43% sample discrimination

(Figure 3b). The wine samples representing the Maule subregion had the highest variability, as they comprise a high diversity of mesoclimates and soils. Maule valley is the largest viticultural origin in Chile with approximately 53,497 ha, representing 36.7% of the national surface area of vineyards dedicated to winemaking (ODEPA, 2016).

As indicated elsewhere (Zou *et al.*, 2012; Versari *et al.*, 2014), the metal composition of wines is a useful way to characterize and discriminate wines according to their geographic area; they largely reflect the composition of metals in the soil and water of the places in which the grapes are grown (Pohl, 2007). The limitations of this technique include the purity of the wines analyzed, variations in winemaking style, the use of winemaking aids, yeast culture and vinification practices, etc. (Pohl, 2007; Rossano *et al.*, 2007; Álvarez *et al.*, 2007; Hopfer *et al.*, 2015). In this case, the samples selected had a limited range of prices and winemaking styles, thus allowing for

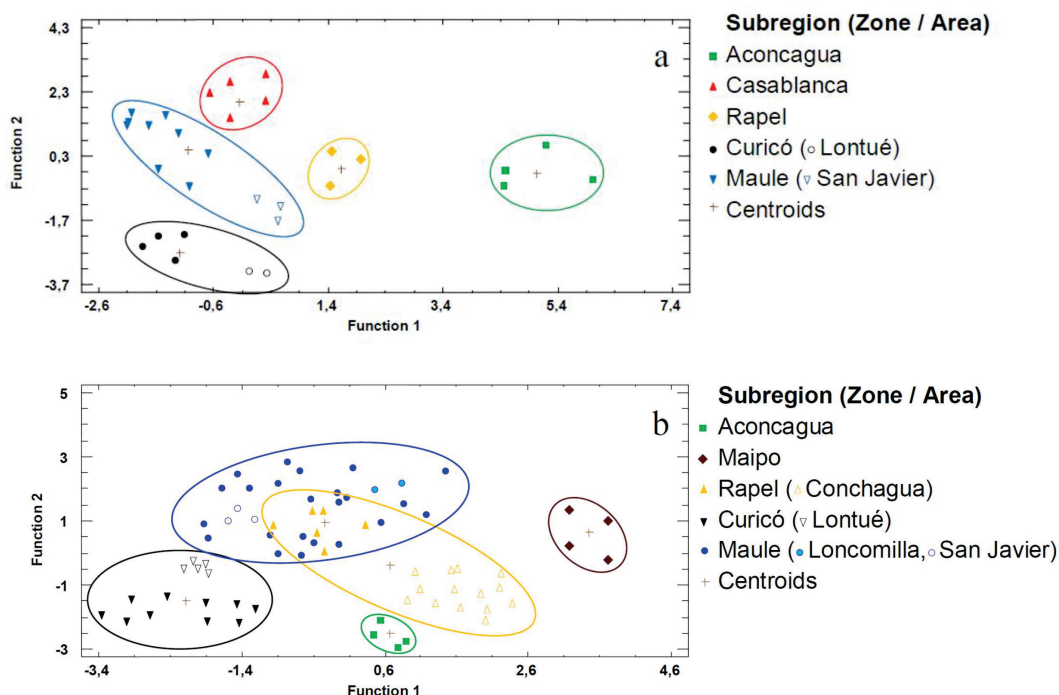


Figure 3. Scatter plot of the linear discriminant functions for (a) 39 samples of white wine analyzed according the region of origin, and (b) 91 samples of red wine analyzed according the region of origin.

a good degree of geographic area discrimination. A more complete study that allows for the determination of the origin of a larger group of wines, the influence of their purity (i.e., unblended vs. blended), production and storage practices, and a greater number of samples per zone is necessary.

The main conclusions are as follows. All metal concentrations were within the ranges previously reported for wines from other regions. As expected, red wines had a higher concentration of K, Mg and Fe compared to white wines, in which Na, Ca, and Zn were particularly concentrated. The exploratory data analysis conducted with PCA allowed for the identification of the main components explaining the variability among samples. In the case of white wines, the first two main components explained 95.28% of the variability, whereas in red wines only 77.69% of the variability was explained by the first two principal components. On the other

hand, LDA analysis allowed for a good degree of discrimination by geographic area for white (i.e., 96.9%) and red wines (i.e., 79.43%). To the best of our knowledge, this is the first time that the content of a large number of metallic elements in Chilean wines has been described and used to discriminate wine origins. No previous attempts to discriminate Chilean wine areas, based on a broad range of multi-elemental compositional data, have been published.

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Resumen

Y. Mirabal-Gallardo, M. A. Caroca-Herrera, L. Muñoz, M. Meneses, y V. F. Laurie. Análisis y diferenciación de vinos chilenos empleando su composición de elementos metálicos y técnicas de estadística multivariada. 2018. Cien. Inv. Agr. 45(2): 181-191. La concentración de diecisiete elementos metálicos se analizó en 130 muestras comerciales de vinos chilenos, utilizando espectroscopía de absorción atómica de llama (AAS) y espectrometría de masas con plasma acoplado inductivamente (ICP-MS). Los elementos analizados estuvieron dentro de los rangos de concentración habituales reportados previamente en otras regiones vitivinícolas del mundo; por ejemplo: Fe, $2,08 \pm 0,99$ mg L⁻¹; Zn, $0,71 \pm 0,44$ mg L⁻¹; K, 788 ± 219 mg L⁻¹; Na, $14,62 \pm 8,6$ mg L⁻¹. Cuando se comparó el contenido metálico de las muestras entre áreas geográficas, se observaron diferencias significativas en la concentración de K, Na, Mn, Mg, Zn y Cr ($p \leq 0.05$). Además, los análisis de componentes principales y análisis discriminación lineal se utilizaron para discriminar los vinos de acuerdo con el área geográfica, obteniendo ajustes por encima del 90 % para los vinos blancos y más del 70 % para los vinos tintos.

Palabras clave: AAS, clasificación, elemento, estadística multivariada, ICP-MS, metal, vino.

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