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QUALITY EVALUATION OF WHITE AND RED WINE VARIETIES, FROM THE MAIN VINEYARDS OF ROMANIA

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The quality of any wine is intrinsically dependent on the quality and composition of the grapes used to produce it. In traditional winemaking countries such as Germany and France, wine quality is determined by geographic origin or the terroir of the wine. The aim of the present research is to determine the quality of wines from the main vineyards of Romania. In terms of quality rating, they display particular characters of the varieties, as well as the ecoclimatic conditions and ecopedological influence on the quality of wine. The work offers new information on the quality of the white wines obtained in main vineyards of Romania, useful for their promotion and marketing. The variation of the physico-chemical characteristics and elemental concentration represents a strong geological marker for wines geographical traceability.

Keywords: metals, quality, wines, *Vitis vinifera*

Introduction

According to the International Organization of Vine and Wine (OIV), wine is a food product exclusively obtained by total/partial fermentation from fresh grapes or the must obtained from pressed/impressed grapes. From the chemical point of view, wines are a complex beverage consisting of water, sugar, amino acids, ethanol, polyphenolic compounds, anthocyanins and organic/inorganic substances (Karataș *et al.*, 2015).

The world of grapes and wines concerns at least 40 counties; the quality and the type of wines depend on natural ecoclimatic conditions and human factors. It said that, worldwide the climate of the different grape growing accounts for large parts of the diversity of varieties cultivated, quality and typenness of the wines and viticultural products (Bora *et al.*, 2016).

Today the grapevine is cultivated worldwide. About 51% of the vine cultivated surfaces of the world is located in Europe, followed by Asia, America and Africa. In Romania the area planted with vines has been reduced since the 1990s, and currently it ranks 5 in Europe after Spain, France, Italy and Portugal. In 2013, Romania had 229 000 ha planted with vines (Bora *et al.*, 2015a).

The wine quality is affected by both cultural and climatic factors, some of which are difficult to evaluate (Jackson *et al*., 1993). The quality of any wine is intrinsically dependent on the quality and composition of the grapes used to produce it. In traditional winemaking countries such as Germany and France, wine quality is determined by geographic origin or the terroir of the wine (Sequin, 1986). Terroir describes the relationship between an agricultural product and its geographical origin and considers that the region of production might influence the products characteristic. In the case of wine, terroir involves the interactions of grapevine, vineyard, ecoclimatic conditions and human factors such as viticultural and oenological practices. More specifically, mesoclimatic variability has to be taken into account, as well as altitude, inclination, orientation and composition of soil. Soil is one of the most important factors of the production area which shows a particular interest for the assessment of the environmental effects on the mineral composition of the wine. In the ongoing effort to develop new monitoring techniques of the wine, geochemical marks significantly improve the traceability of wines to their origins, especially the mineral compositions of wines. Together, the various aspects of terroir affect the development and composition of the grapes, which in turn influences the characters of the wine, so terroir can be seen as a proxy for wine quality.

The aim of our research was therefore to (1) evaluate the quality of white and red wine varieties from the main vineyards of Romania, (2) determination of total metal concentration from wines samples (3) establishing some Pearson correlation coefficient between quality parameters of wine and between the determined elements, (4) determination of wine geographical traceability amongst physico-chemical parameters and metal concentration from wines samples.

Materials and methods

Study area

A total of 84 wine samples were analyzed (2 red wines varieties (Fetească neagră, Merlot) and 2 white wines varieties (Sauvignon blanc, Fetească regală)). Samples originated from five different Romanian vineyard: Dealu Bujorului vineyard (45°52′10″ N-27°55′8″E) (n = 24), Murfatlar vineyard (44°10′25″ N-28°24′30″ E) (n = 12), Tarnava vineyard (46°10′31″ N-23°54′52″ E) (n = 12), Iasi vineyard (47°9′44″ N-27°35′20″ E) (n = 12) and Ștefănești-Argeș vineyard (44°51′53″ N-24°57′0″ E) (n = 24). The regions differ in geographical features and also by soils geological/pedological patterns. The Dealu Bujorului region is characterized by an alternate landscape, from flat to hilly areas, with altitude between 100 and 225 m and the predominant soil is levigated chernozem with a clayey sand texture and pH of 7.5 - 8.0. The Murfatlar region landscape is characterized by high fragmentation; with altitude between 0 and 100 m and the predominant soil is chernozem having clayey sand texture with pH values between 7.6 and 8.3. The Tarnava vineyard is situated on the southern slopes and stating at the altitude of 250-270 m up to 400-450 m, the slope of these lands being between 15-35%. The largest slopes are situated on the river Tarnava Mare and descend on Tarnava Mica, Mures and the inner valleys. Predominant soil was aluvisol with pH between values 7.6 and 8.3. Iasi vineyard are represented by fragmented hills with low sloping plateaus, as a result of the erosion action with altitude between 100 and 200 m and the predominant soil is chernozems with pH values between 5.3-8.0. On the other hand, the landscape of Ștefănești-Argeș vineyard is very billowy terrain with altitude between 200 and 412 m and the predominant soil is protisols with pH 6.6-7.9.

Sample collection and microvinification process

The wine samples used were obtained from Sauvignon blanc, Feteasca regala, Feteasca neagra and Merlot wines under the conditions of 2015 and 2016 year, from Dealu Bujorului, Murfatlar, Tarnava, Iași and Ștefănești-Argeș vineyard. Around 4-5 kg of grapes / cultivar was collected from 10 vines / replication. Three repetitions / cultivar were used, placed in randomized blocks. The wine samples resulted from micro-wine production. Micro-vine production it was done according to the methodology described by Bora *et al.* (2016). All wines were providing by the wineries as finished wines in 750 mL glass bottles with cork stoppers and were stored at 3-4 ^{0}C before analysis. One bottle was used for each sample, and three replicates were taken. All the vines were planted from 1979, and the vine plantation was organized with 2.2 x 1 m distance between plants and rows. Vines were planted according to the Guyot system and were grown on speliers.

Reagents and solutions

All chemicals used in the experiment were of analytical grade. For the physico-chemical analyses of wine we used Sigma-Aldrich chemicals. High purity ICP-MS multielement standard solution XXI CertiPUR obtained from Merck was used for calibration curve in the quantitative analysis. Standard solution of metals K, Na, Ca, Mg, Fe, Cu, Mn, Zn and Li 1000±0.002 mg/L were used. The control sample and working standards were freshly prepared for the experiments out of the stock solution. The accuracy of the methods was determined by running replicate analyses and the obtained values ranged, for different elements, between 0.8 and 13.1%. The global recovery of the elements varied between 85.6-101.3%.

Blanks and triplicate samples (n = 7) were considered in the experiment for each procedure. The variation coefficient was under 4%. The calibration curves were used to determine the detection limits (ppb) for each method. Limit of quantification (LoQ) and Limit of detection (LoD) were calculated as follows: LoQ

= 10 SD/s and LoD = 3SD/s, where SD is the estimation of the standard deviation of the regression line while s is the slope of the calibration curve.

Table 1. Conditions for the determination of each element (ICP-MS) technique

Element	Correlation coefficient	LoD* (µg/L)	LoQ*** (µg/L)	BEC** (µg/L)
K	0.9999	2.1860	7.2794	31.728
Na	0.9999	3.9808	13.2561	32.121
Ca	0.9999	5.6649	18.8641	20.820
Mg	0.9999	2.7325	9.0992	9.099
Fe	0.9999	5.2102	17.3500	71.399
Cu	0.9993	0.0401	0.1337	0.237
Mn	0.9999	0.0102	0.0340	0.085
Zn	0.9999	0.3780	1.2587	5.401
Li	0.9999	0.0048	0.0160	0.020

*Detection limit; **Background equivalent concentration; ***Quantification limit.

Sample preparation for determination of heavy metals from wine

The physico-chemical analyses of wine were performed in the Laboratory of Winemaking of the RSDVV Bujoru; these methods of analysis were described in (Postolache et al., 2016). In order to determine the heavy metals from wine samples, a volume of 0.2 mL wine was mixed with 1 mL H_2O_2 and 7 mL HNO_3 69% and after 15-30 minutes the mineralization was performed in three steps using a microwave system Milestone START D Microwave Digestion System as follows: step I - 10 min. at 200ºC, step II - 15 min. at 200ºC and step III - 60 min. under ventilation at 35ºC. Afterwards all samples were filtered through a 0.45 mm filter and diluted to 50 mL.

Equipments

In this case the pH was measured with WTW inoLab pH 7110. For determination of physico-chemical characteristics of red wine we used UV-VIS spectrometer (SpectronicHelios Gamma UV-Vis, ThermoFisher Scientific). A mass spectrometer with inductively coupled plasma (ICP-MS) iCAP Q Thermo scientific was used to determine the metals. The experimental conditions used for measurement were: argon flow on nebulizer (0.84 L/min.), auxiliary gas flow 0.80 L/min., argon flow in plasma 15 L/min., lens voltage 7.31 V; RF power in plasma 1100 W, spray chamber temperature (2.51±1.00 ºC). Accuracy was calculated for the elements taken into consideration (0.5-5.0%).

Statistical analysis

The statistical interpretation of the results was performed using the SPSS, version 24 (SPPS Inc. Chicago, IL, USA). The following statistical parameters were determined: average error, standard deviation, arithmetic average, using the SPSS version 24 (SPPS Inc. Chicago, IL, USA). In order to determine whether the main quality parameters of wine can influence each other, the correlation coefficient was calculated using SPSS version 23 Pearson (SPSS Inc., Chicago, IL., USA). Linear discriminant analysis (LDA) was performed in order to separate the wines by region and to indentify the markers with a significant discrimination value (variables with Wilk's lambda near zero, *p* values <0.005 and higher F coefficients). Linear discriminant analysis (LDA) was performed using Microsoft Excel 2016 and XLSTAT Addinsoft version 15.5.03.3707.

Results and discussion

Physico-chemical characteristics of wines samples

When analyzing each wine variety can be noted that the obtained wine presented are variable alcohol content. Vine varieties for red wine recorded the highest values for alcohol content [15.51±0.38 (% vol.); 15.40±0.14 (% vol.) Merlot Dealu Bujorului and 14.89±0.38 (% vol.); 14.71±0.10 (% vol.) Feteasca neagra Ştefãneşti-Argeş vineyard], vine varieties for white wine recorded the highest values for alcohol content in Sauvignon blanc growing in Ştefãneşti-Argeş vineyard [13.37±0.17 (% vol.) 2015; 12.54±0.12 (% vol.) 2016], followed by Sauvignon blanc from Dealu Bujorului vineyard [12.41±0.19 (% vol.) 2015; 12.48±0.03 (% vol.) 2016]. The lowest values of alcoholic strength were recorded in varieties grown in Murfatlar vineyard. The analyzed wines have a high alcoholic potential, being within the normal range between (10.71 to 13.37 % vol. white wines) and (13.49 to 15.51 % vol. red wines). The results are comparable with the results reported by de Bruijn *et al.*, 2014 (13.30±0.10 [% vol.], 12.30±0.10 [% vol.] Sauvignon Blanc wines), Miličević *et al.*, 2014 (13.20±0.10 [% vol.] Syrah), Trigo-Córdoba *et al.*, 2015 (13.60±0.00 [% vol.] Godello [white wine], and Baiano *et al.*, 2015 (11.44±0.11 [% vol.] Nero din Troia [red wine]).

Regarding total acidity (g/L $C_4H_8O_6$), vine varieties for white wines grown in Târnava vineyard Sauvignon blanc [7.50±0.01 g/L $C_4H_8O_6$ (2015)] and Iaşi vineyard Feteasca regala [7.70±0.22 g/L $C_4H_8O_6$ (2016)] recorded the highest values for total acidity, while varieties grown in Dealu Bujorului, Murfatlar and Ştefãneşti-Argeş recorded lower values. On the opposite pole Feteasca neagră from Dealu Bujorului [9.19±0.09 g/L $C_4H_8O_6$ (2015)] and Merlot [8.83±0.01 g/L $C_4H_8O_6$ (2015)] recorded the highest values, followed by Merlot from Ştefãneşti-Argeş [7.28±0.07 g/L $C_4H_8O_6$ (2016)]. The results are comparable with data obtained by Budić-Leto *et al.*, 2009 (4.68±0.03 [g/L $C_4H_6O_6$]), and Miličević *et al.*, 2014 (5.50 ± 0.15 [g/L $C_4H_6O_6$] Syrah).

Varieties grown in Murfatlar vineyard recorded the lowest values for volatile acidity [0.31±0.02 g/L CH_3COOH (2015); 0.38±0.03 g/L CH_3COOH (2016) recorded by Sauvignon blanc and 0.33±0.02 g/L CH_3COOH (2015); 0.36±0.03 g/L CH_3COOH (2016) recorded by Feteasca regala], while Sauvignon blanc from Ştefãneşti-Argeş [0.51±0.01 g/L CH_3COOH (2015)] recorded de highest values, from white wines. Merlot varieties from Dealu Bujorului [0.72±0.01 g/L CH_3COOH (2015); 0.65±0.03 g/L CH_3COOH (2016)] and Feteasca neagra from Ştefãneşti-Argeş [0.62±0.01 g/L CH_3COOH (2015); 0.63±0.02 g/L CH_3COOH (2016)] recorded the highest values. Between the analyzed variants there are significant differences. The results are comparable with those reported by Bruijn *et al.*, 2014 (0.50±0.00 [g/L CH_3COOH], 0.40±0.00 [g/L CH_3COOH] Sauvignon Blanc wines), Miličević *et al.*, 2014 (0.46±0.20 [g/L CH_3COO]) Syrah), and greater than those obtained by Baiano *et al.*, 2015 (0.12±0.01 [g/L CH_3COO]).

In case of non-reducible extract, the lowest values was recorded by Sauvignon blanc from Ştefăneşti-Argeş [19.07±0.25 g/L (2015); 19.09±0.30 g/L (2016)], followed by Sauvignon blanc from Târnavelor vineyard [19.48±0.16 g/L (2015)] and Feteasca regala from Iaşi [19.65±0.06 g/L (2016)]. Regarding red wines, Merlot variety from Ştefăneşti-Argeş [24.54±0.41 g/L (2015); 25.58±0.34 g/L (2016)] recorded the lowest values. On the opposite pole Sauvignon blanc (2015), Feteasca regala (2015) and Feteasca neagra (2015), Merlot (2015) from Dealu Bujorului recorded the highest non-reducible extract. The results are comparable with those reported by Bora *et al.*, 2016 (29.00±0.50 [g/L Muscat Ottonel], 20.00±1.00 [g/L Feteasca alba], 27.0±01.00 [g/L Sauvignon blanc], 21.10±1.00 [g/L Aligoté]).

The sugar content values vary within large range [Dealu Bujorului, Sauvignon blanc 10.49±0.15 g/L (2015); Feteasca neagra 10.40±0.10 g/L (2016)] to [Dealu Bujorului, Merlot 36.89±0.05 g/L (2015); 10.40±0.04 g/L (2016)]. The lowest values were recorded by Feteasca regala from Ştefăneşti-Argeş [1.48±0.02 g/L (2015); 1.17±0.15 g/L (2016)] to [0.73±0.64 g/L (2016) Feteasca regala from Iaşi vineyard]. The wines under study fall into the category of dry, semi-dry and semi-sweet wines. The results are comparable with those reported by Bora *et al.*, 2016 (30.70±0.75 [g/L Muscat Ottonel], 23.00±1.00 [g/L Şarba], 12.0±5.00 [g/L Sauvignon blanc], 72.00±1.00 [g/L Italian Riesling]), and higher than Miličević *et al.*, 2014 (2.85±0.25 [mg/L, Syrah].

The highest pH was obtained in the wine produces from Sauvignon blanc from Murfatlar vineyard [3.66±0.01 (2015)], followed by Sauvignon bl2anc from Ştefăneşti-Argeş vineyard [3.75±0.01 (2015)] and Merlot blanc from Ştefăneşti-Argeş [3.77±0.02 (2015)]. Feteasca regala variety from Iaşi vineyard recorded the lowest pH values [2.86±0.14 (2016)] and Feteasca neagra variety from Ştefăneşti-Argeş vineyard [3.07±0.01 (2015)]. The results are comparable with those reported by Bora *et al.*, 2016 (3.47±0.10 [Muscat Ottonel], 3.32±0.17 [Şarba], 3.54±0.17 [Sauvignon blanc], 3.46±0.01 [Italian Riesling]), and also with those reported by Bora *et al.*, 2016b (3.30±0.01 [Merlot].

In the case of free SO_2, white wines recorded the highest values at Feteasca regala [40.71±0.02 mg/L (2015) Murfatlar vineyard], followed by the Sauvignon blanc [39.50±1.57 mg/L (2016) Murfatlar vineyard] and at the opposite pole with the lowest free SO_2 was Feteasca regala [21.40±0.84 mg/L (2015) Ştefăneşti-Argeş vineyard] followed by the Feteasca regala [22.61±1.51 mg/L (2015) Iaşi vineyard]. By comparing vines for white wine with varieties of red wine, one can get tired of the fact that the vines for red wines have a low content of free SO_2. The wines obtained in Ştefăneşti-Argeş vineyard recorded the highest [Feteasca neagra 31.26±1.28 mg/L (2015)] followed by the [Merlot 31.62±0.28 mg/L (2015)]. Analyzing the results in terms of free SO_2 content, it can be seen that all wines have a much lower content than the one required by low, therefore the wine can be preserved or consumed.

The highest total SO_2 content was recorded in wines from Murfatlar vineyard [Sauvignon blanc 179.13±0.61 mg/L (2015); Sauvignon blanc 138.84±9.41 mg/L (2016)] and [Feteasca regala 179.45±1.73 mg/L (2015)] followed by the Sauvignon blanc [137.00±4.26 mg/L (2016) Ștefănești-Argeș vineyard]. The Sauvignon blanc variety from Ștefănești-Argeș vineyard [50.44±1.86 mg/L (2015)] and Feteasca regala from Iași vineyard [64.83±1.36 mg/L (2015)] were recorded the lowest concentration of total SO_2. In this case, the red wine also recorded lower values. The highest concentration of total SO_2 was recorded in Merlot [85.11±1.51 mg/L (2016), Dealu Bujorului vineyard and 81.13±2.40 mg/L (2016) Ștefănești-Argeș vineyard]. The results are comparable with those reported by Bora *et al.*, 2016 (60.00±1.20 [mg/L Free SO_2 Muscat Ottonel], 52.32±0.60 [Șarba mg/L Free SO_2], 20.00±0.61 [Sauvignon blanc mg/L Free SO_2], 18.00±0.30 [Italian Riesling mg/L Free SO_2]), and by Bora *et al.*, 2016 (240.00±6.40 [mg/L Total SO_2 Muscat Ottonel], 217.00±1.00 [Șarba mg/L Total SO_2], 163.00±1.00 [Sauvignon blanc mg/L Total SO_2], 208.00±2.00 [Italian Riesling mg/L Total SO_2]).

Regarding the color intensity of the tested wines, based on the results, we can state that the highest color tint was recorded in the Feteasca neagra variety from Dealu Bujorului vineyard [9.097±0.057 (2015); 8.941±0.042 (2016)], compared to the same variety grown in Ștefănești-Argeș vineyard [8.320±0.026 (2015); 7.865±0.069 (2016)]. The results are comparable with those reported by Bora *et al.*, 2016b (8.740±0.060 [Merlot], 7.700±0.030 [Cabernet Sauvignon], 8.380±0.090 [Feteasca Neagra]).

The highest concentration color tint was recorded in Feteasca neagra from Ștefănești-Argeș vineyard [0.877±0.350 (2015) and 0.817±0.021 (2016)] compared to the same variety grown in Dealu Bujorului [0.793±0.001 (2015) and 0.784±0.002 (2016)]. Regarding Feteasca neagra, Merlot variety from Dealu Bujorului vineyard and Merlot variety from Ștefănești-Argeș vineyard there is not statistical difference between the analyzed variants. The results are comparable with those reported by Bora *et al.*, 2016b (0.810±0.040 [Merlot], 0.690±0.020 [Cabernet Sauvignon], 0.740±0.020 [Feteasca Neagra]).

In case of total polyphenols, the lowest values were recorded by wine from Ștefănești-Argeș vineyard [Feteasca neagra 0.88±0.04 g/L (2015) and 2.08±0.17 g/L (2016)]; [Merlot 0.78±0.01 g/L (2015) and 1.94±0.06 g/L (2016)] compared to the same variety grown in Dealu Bujorului vineyard [Feteasca neagra 2.04±0.02 g/L (2015) and 2.26±0.04 g/L (2016)]; [Merlot 2.08±0.02 g/L (2015) and 2.02±0.07 g/L (2016)]. The results are comparable with those reported by Bora e*t al.*, 2016b (1.29±0.01 [g/L Merlot], 1.14±0.02 [g/L Cabernet Sauvignon], 1.28±0.01 [g/L Feteasca Neagra]).

Just like in case of total polyphenols, the anthocyanis recorded the lowest values at wine from Ștefănești-Argeș vineyard [Feteasca neagra 407.92±1.25 g/L (2015) and 489.62±19.71 g/L (2016)]; [Merlot 316.81±0.61 g/L (2015) and 418.33±16.96 g/L (2016)] compared to the same variety grown in Dealu Bujorului vineyard [Feteasca neagra 913.67±4.04 g/L (2015) and 621.87±11.99 g/L (2016)]; [Merlot 663.44±7.05 g/L (2015) and 502.56±6.88 g/L (2016)]. The results are comparable with those reported by Bora *et al.*, 2016b (302.67±2.08 [g/L Merlot], 216.33±1.53 [g/L Cabernet Sauvignon], 281.33±1.53 [g/L Feteasca Neagra]).

Total metal concentration from wines samples

As expected potassium was the most abundant element in all investigated red and white wine samples since this element is essential for the growth and development of plants and is often a component of fertiliser (Rodrigues *et al*., 2011). The vine requires high contents of potassium for its mineral nutrition, which can be further found in must and wine. According to Ţârdea *et al.* (2001) Potassium is responsible for the finesse of the wine, while the low potassium samples have a harsh taste. The highest concentration of Potassium was recorded in the wine samples from Dealu Bujorului vineyard [Merlot 485.79±2.14 mg/L (2015); 489.38±0.21 mg/L (2016)] followed by Feteasca neagra [335.97±7.09 mg/L (2015); 326.70±4.99 mg/L (2016)] and Merlot [291.12±5.49 mg/L (2015)] from Ștefănești-Argeș vineyard. Among the analyzed variants was a very significant difference ($F = 54.115$; $p \leq 0.000$). The polyfactorial analysis indicated that the area of vineyard culture significantly influences the accumulation of K in wines ($F = 5.732$; $p \leq 0.000$), while the variety and the interaction between area of culture and had no significant influence on this character. These results are lower compared to the values reported in the literature (Iglesias *et al.*, 2007 - average values of 819.61 mg/L; Álvarez *et al.*, 2012 - average values of 865.30 mg/L), and agree with those reported by Bora *et al.*, 2008 [Feteasca alba 323.26±3.25 mg/L (2014)], [Feteasca regala 235.86±10.25 mg/L (2014)].

The highest Sodium concentration was found in wine sample from Dealu Bujorului vineyard [Feteasca neagra 51.82±0.98 mg/L (2016)] followed by wine from Murfatlar vineyard [Feteasca regala 46.01±1.32 (2015)].

Feteasca regala variety from Dealu Bujorului vineyard [22.41±0.90 mg/L (2015)] and Merlot variety from Ștefănești-Argeș vineyard [25.55±1.49 mg/L (2015)]. When comparing the average value (37.37 mg/L Na) to the ones reported in the legislation, one can notice that the concentrations of Na are below the allowed maximum limit (60 mg/L). The Na content in our study are similar with the results published on Serbian (Ražić and Onjia, 2010 average values of 29.65 mg/L Na), Czech (Kment *et al.*, 2005 average values of 14.7 mg/L Na) and Spanish (Iglesias *et al.*, 2007 average values of 37.19 mg/L Na) wines.

The large amounts of calcium present in wines can be due to some exogenous sources, treatment with bentonite, filtration with alluvial infusorial soil (diatomite), storage of wine in concrete tanks, and de-acidification of calcium carbonate. Low temperature and pH values of 2.9-3.2 favor TCa crystals formation because tartrate anions (T2-) rise when combines with the calcium in wine. On the other hand, at high temperature the formation of calcium malate is favored (Bora *et al.*, 2015b).

Table 2. Physico-chemical characteristics of white wines (Sauvignon blanc and Fetească regală) (n = 3)

Area/Vineyard	Variety	Year	Alcohol (% vol.)	Total acidity (g/L $C_4H_8O_6$)	Volatile acidity (g/L CH_3COOH)	Non-reducible extract (g/L)	Sugar content (g/L)	pH	Free SO_2 (mg/L)	Total SO_2 (mg/L)
			Parameters Analyzed							
Dealu Bujorului	Sauvignon blanc	2015	12.41±0.19 bc	6.79±0.10 b	0.45±0.02 b	24.67±1.43 a	10.49±0.15 a	3.32±0.03 b	20.18±0.11 d	95.84±1.98 e
		2016	12.48±0.03 bc	5.72±0.13d	0.27±0.02 d	19.65±0.34c	[1]SLD h	3.39±0.04 b	22.39±1.10 d	83.65±2.52 f
	Fetească regală	2015	12.73±0.27 b	6.11±0.02 dc	0.27±0.02 d	22.48±0.14 a	[1]SLD h	3.36±0.02 bc	17.74±1.85 c	74.7±2.39 fg
		2016	12.29±0.08 bc	6.49±0.13 b	0.46±0.01 b	21.45±0.23ab	10.40±0.10 a	3.25±0.06 c	30.78±1.85 c	102.08±2.78 d
Murfatlar	Sauvignon blanc	2015	11.54±0.34 cd	5.51±0.02 d	0.31±0.02 c	20.26±0.09 bc	1.51±0.02 f	3.66±0.01 a	30.71±0.02 c	179.13±0.61 a
		2016	12.30±0.03 b	6.53±0.10 b	0.38±0.03 c	22.59±0.12b	4.80±0.80 c	3.28±0.08 c	39.50±1.57a	138.84±9.41 a
	Fetească regală	2015	10.71±0.35 d	6.30±0.02 bc	0.33±0.02 c	19.73±0.10c	4.04±0.02 c	3.58±0.01 ab	40.71±0.02 a	179.45±1.73 a
		2016	11.52±0.10 cd	6.41±0.05 b	0.36±0.03 c	21.45±0.05 b	2.31±0.11 e	3.17±0.07 cd	35.15±1.01b	124.34±5.20bc
Târnavelor	Sauvignon blanc	2015	11.51±0.01 cd	6.41±0.01 b	0.32±0.02 c	19.48±0.16c	1.46±0.07 f	3.11±0.02 cd	22.49±0.17 d	137.79±1.74 b
		2016	11.83±0.25 c	6.35±0.14 bc	0.40±0.04b	21.47±0.61 ab	5.48±0.76b	3.10±0.02 d	30.99±1.47 c	128.52±1.99 b
	Fetească regală	2015	11.55±0.07 cd	7.50±0.01 a	0.37±0.02 c	20.35±1.07 bc	7.55±0.06 b	3.04±0.03 d	17.51±0.07 e	97.46±1.13 e
		2016	11.21±0.10 cd	6.30±0.18 bc	0.33±0.03 c	20.48±0.16 bc	1.48±0.18 fg	3.12±0.16 cd	25.63±1.18 d	113.48±3.11 c
Iași	Sauvignon blanc	2015	11.33±0.11 cd	6.12±0.02 c	0.46±0.01 b	20.02±0.06bc	2.56±0.03 e	3.62±0.01 ab	24.25±0.33 d	102.30±1.07 d
		2016	12.03±0.32 bc	7.60±0.10 a	0.50±0.03a	20.04±0.04 bc	1.20±0.20 g	2.99±0.11de	23.46±0.78 d	94.23±1.22 ef
	Fetească regală	2015	12.33±0.21 bc	6.13±0.02 c	0.48±0.03 b	21.06±0.03 ab	1.76±0.05 f	3.51±0.02 ab	32.30±0.84 c	64.83±1.36 g
		2016	11.25±0.22 c	7.70±0.22 a	0.47±0.03 b	19.65±0.06 c	0.73±0.64 i	2.86±0.14 f	22.61±1.51 d	86.49±1.49 f
Ștefănești-Argeș	Sauvignon blanc	2015	13.37±0.17 a	6.58±0.22 b	0.51±0.01 a	19.67±0.25 c	3.43±0.10 d	3.75±0.01 a	34.57±1.00 b	50.44±1.86 h
		2016	12.54±0.12 bc	6.32±0.09 bc	0.46±0.04 b	19.09±0.30 cd	3.40±0.20 d	3.25±0.07 bc	35.22±0.07 b	137.00±4.26 a
	Fetească regală	2015	11.33±0.34 cd	6.06±0.03 c	0.41±0.01 b	20.15±0.69b	1.48±0.02 fg	3.59±0.03 ab	21.40±0.84 h	107.61±1.30 d
		2016	11.90±0.15 c	6.89±0.15 b	0.35±0.03 c	19.00±0.12 d	1.17±0.15 h	3.35±0.09 bc	29.93±1.62 cd	119.73±2.61 c
	Sig.		***	***	***	***	***	**	***	***

Average value ± standard deviation (n = 3). Romans letters represent the significance of the variety difference ($p \leq 0.05$). The difference between any two values, followed by at least one common letter, is insignificant.

Table 3. Physico-chemical characteristics of red wines(Fetească neagră and Merlot) (n = 3)

Area/Vineyard	Variety	Year	Alcohol (% vol.)	Total acidity (g/L $C_4H_8O_6$)	Volatile acidity (g/L CH_3COOH)	Non-reducible extract (g/L)	Sugar content (g/L)	pH
Dealu Bujorului	Fetească neagră	2015	14.84±0.82 b	9.19±0.09 a	0.56±0.06 b	33.70±1.80 a	5.76±0.16 c	3.46±0.04 b
		2016	14.60±0.10 b	8.50±0.10 b	0.58±0.02 b	31.23±0.15 b	4.56±0.15 c	3.34±0.03 bc
	Merlot	2015	15.51±0.38 a	8.83±0.01 b	0.72±0.01 a	36.18±0.28 a	36.89±0.05 a	3.31±0.02 bc
		2016	15.40±0.14 a	8.53±0.15 b	0.65±0.03 a	32.70±0.16 b	10.40±0.04 b	3.23±0.03 b
Ștefănești-Argeș	Fetească neagră	2015	14.89±0.38 b	6.44±0.05 d	0.62±0.01 a	28.36±0.24 c	2.65±0.09 d	3.07±0.01 c
		2016	14.71±0.10 b	6.69±0.14 d	0.63±0.02 a	26.28±0.53 d	2.63±0.06 d	3.42±0.09 b
	Merlot	2015	13.49±0.20 c	6.83±0.07 d	0.53±0.02 c	24.54±0.41 e	1.89±0.11 e	3.77±0.02 a
		2016	13.49±0.02 c	7.28±0.07 c	0.54±0.02 c	25.58±0.34 f	1.87±0.14 e	3.32±0.10 bc
Sig.			***	***	***	***	***	*

Area/Vineyard	Variety	Year	Coloring intensity	Color tint	Total polyphenols (g/L)	Anthocyanis (g/L)	Free SO_2 (mg/L)	Total SO_2 (mg/L)
Dealu Bujorului	Fetească neagră	2015	9.097±0.057 a	0.793±0.001 b	2.04±0.02 a	913.67±4.04 a	12.72±0.14 d	64.34±1.13 c
		2016	8.941±0.042 a	0.784±0.002 b	2.26±0.04 a	621.87±11.99 b	22.29±0.94 c	88.48±0.76 a
	Merlot	2015	8.707±0.009 b	0.777±0.011 b	2.08±0.02 a	663.44±7.05 b	12.90±0.13 d	65.33±0.95 c
		2016	8.788±0.084 b	0.770±0.010 b	2.02±0.07 ab	502.56±6.88 c	25.88±1.59 b	85.11±1.41 a
Ștefănești-Argeș	Fetească neagră	2015	8.177±0.015 c	0.877±0.350 a	0.88±0.04 d	407.92±1.25 c	31.26±1.28 a	35.05±2.12 d
		2016	7.786±0.156 d	0.817±0.021 a	2.08±0.17 ab	489.62±19.71 d	22.77±1.52 b	79.54±0.71 b
	Merlot	2015	8.320±0.026 c	0.786±0.034 b	0.78±0.01 d	316.81±0.61 f	31.62±0.82 a	48.32±0.86 c
		2016	7.865±0.069 d	0.720±0.020 b	1.94±0.06 c	418.33±16.96 e	23.25±1.20 b	81.13±2.40 a
Sig.			***	***	**	***	**	*

Average value ± standard deviation (n = 3). Romans letters represent the significance of the variety difference ($p \leq 0.05$).
The difference between any two values, followed by at least one common letter, is insignificant.

The highest concentration of Ca was recorded in wine from Iași vineyard by Sauvignon blanc variety [78.22±3.64 mg/L (2015); 78.47±1.27 mg/L (2016)] and Feteasca regala variety from Ștefănești-Argeș vineyard [82.34±1.92 mg/L (2015)]. In case of Mg concentration, wine from Târnavelor vineyard [Sauvignon blanc 144.42±2.71 mg/L (2016)], from Iași vineyard [Feteasca regala (131.15±6.98 mg/L (2015)] and Ștefănești-Argeși vineyard [Sauvignon blanc 145.29±3.82 mg/L (2016) and Feteasca regala 136.49±3.74 mg/L (2015); 141.95±8.02 mg/L (2016)] recorded the highest concentration of Mg.

The values obtained for the Mg and Ca contents in our selected wines were in good agreement with the results for Macedonian (Ivanova-Petropulos *et al.*, 2013 average values of 83.5 mg/L Ca and 98.20 mg/L Mg), Serbian (Ražić and Onjia, 2010 - average values of 37 mg/L Ca and 95.73 mg/L Mg), Croatian (Vrček *et al.*, 2011 - average values of 65.90 mg/L Ca and 68.70 mg/L Mg) and also Czech wines (Kment *et al.*, 2005 - average values of 108.00 mg/L Ca and 75.40 mg/L Mg). On the other hand, our Ca and Mg contents were significantly higher than published data for wines from Argentina (Lara *et al.*, 2005 average values of 12.50 mg/L Ca) and Belgium (Coetzee *et al.*, 2014 average values of 6.73 mg/L Ca and 12.05 mg/L Mg).

Sauvignon blanc from Dealu Bujorului vineyard [3.49±0.54 mg/L (2015); 3.58±0.43 mg/L (2016)], from Murfatlar vineyard [3.58±0.43 mg/L (2016)] and also from Ștefănești-Argeș vineyard [3.25±0.67 mg/L (2016)] recorded the highest concentration of Fe. In terms of Fe concentration in red wine, the recorded concentration are within normal limits, Dealu Bujorului vineyard [Feteasca neagra 1.86±0.62 mg/L (2015); 1.74±0.10 mg/L (2016); Merlot 2.10±0.65 mg/L (2015); 2.13±0.01 mg/L (2016)] and Ștefănești-Argeș [Feteasca neagra 1.86±0.62 mg/L (2015); 2.92±1.01 mg/L (2016); Merlot 2.11±0.32 mg/L (2015); 1.90±0.69 mg/L (2016)].

Cu concentration was within wide limits, recorded the highest concentration of Cu were recorded in wine from Dealu Bujorului vineyard [Feteasca regala 0.92±0.03 mg/L (2016)] and in wine from Murfatlar vineyard [Feteasca regala 0.94±0.03 mg/L (2016)]. Sauvignon blanc variety from Târnava vineyard [3.36±0.05 mg/L (2015); 0.35±0.05 mg/L (2016)] and Feteasca regala from Iași vineyard [0.31±0.08 mg/L (2015)] recorded the lowest concentration of Cu in wine sample. Anyway, the values of Na concentration are below the maximum limit allowed by the applicable law (1 mg/L).

For the nutrition of vines, manganese is a microelement that it takes from soil and accumulates in grapes at very low concentrations. The highest concentration of Mn in wine were recorded in wine from Dealu Bujorului vineyard [Feteasca regala 0.61±0.09 mg/L (2016); Feteasca neagra 0.52±0.15 mg/L (2016)], followed by Feteasca regala from Murfatlar vineyard [0.61±0.09 mg/L (2016)], Feteasca regala from Tarnava vineyard [0.54±0.13 mg/L (2016)] and also Feteasca regala from Ștefănești-Argeș vineyard [0.58±0.08 mg/L (2016)]. Low concentration were recorded in wine from Dealu Bujorului vineyard [Feteasca neagra 0.17±0.02 mg/L (2015); Merlot 0.21±0.08 mg/L (2015) and 0.25±0.06 mg/L (2016)] and Murfatlar vineyard [Sauvignon blanc 0.29±0.06 mg/L (2015) and 0.27±0.02 mg/L (2016)].

Statistical analysis indicated significant differences between the analyzed variants (F = 2.828; $p \leq 0.041$).
The highest concentration of Zn in wine were recorded in wine from Dealu Bujorului vineyard [Feteasca regala 3.16±0.05 mg/L (2015); 3.06±0.09 mg/L (2016)] and wine from Murfatlar vineyard [Feteasca regala 4.01±0.19 mg/L (2015)]. Sauvignon blanc variety from Ștefănești-Argeș [1.05±0.16 mg/L (2015); 1.00±0.02 mg/L (2016)], Feteasca regala [1.11±0.09 mg/L (2015)] and Merlot [0.73±0.16 mg/L (2015)] from the same vineyard recorded the lowest concentration of Zn in wine sample. Zn concentration was within wide limits [4.01±0.19 mg/L maximum value] to [0.73±0.16 mg/L minimum value] with an average value of [1.08 mg/L Zn]. Based on the statistical analysis, it can be observed that the between analyzed variants are distinctly significant difference (F = 17.550; $p = 0.000$). The average value (1.85 mg/L) of Zn concentrations is below the maximum limit allowed by the law (5 mg/L).
The behavior of Li in wine resamble that of alkaline-earth metals and particularly the one of Mg. When aging the bottled wine, a reducing environment is created, causinf the lithium to be expelled out of the wine. The highest concentration of lithium in wine were recorded in wine out of Dealu Bujorului vineyard [Feteasca regala 14.15±0.47 mg/L (2015); Feteasca neagra 14.67±0.35 mg/L (2015); 14.98±1.17 mg/L (2016)], wine from Murfatlar vineyard [Feteasca regala 13.58±1.04 mg/L (2015)], wine from Iași vineyard [Feteasca regala 13.09±1.35 mg/L (2016)] and also wine from Ștefănești-Argeș vineyard [Sauvignon blanc 13.31±1.02 mg/L (2015); 13.31±1.68 mg/L (2016)], [Feteasca neagra 14.00±0.23 mg/L (2015); 13.03±2.53 mg/L (2016)]. Low concentration were recorded in wine from Iași vineyard [10.71±1.44 mg/L (2015)] followed by wine from Târnava vineyard [Sauvignon blanc 11.31±0.98 mg/L (2015); 11.39±1.96 mg/L (2016)].
Cu, Mn, Zn, and Li were also present in amounts similar to previously published results (Pohl 2007; Fabani *et al.*, 2010; Di Paola-Naranjo *et al.*, 2011; Ivanova-Petropulos *et al.*, 2013; Avram *et al.*, 2014; Catarino *et al.*, 2014; Geana *et al.*, 2016).
This higher content of some metals may be due to the viticultural practices, the use of fertilizers for cultivation of vine (K, Ca, Cu) the winemaking process or addition of substances for wine clearing as bentonite (Na, Ca, Fe). Cu content is below the limit of detection due to the modern technology for obtaining wines in a controlled manner.

The Pearson correlation between the main parameters analysed in wine

In order to determine whether the main quality parameters of wine can influence each other, the Pearson correlation coefficient was calculated for each studied parameter as it shown in Table 4 and 5. A Pearson correlation coefficient value higher than 0.5 shows a strong correlation between the analysed varieties, a positive correlation between the two parameters shows that both parameters increased, a negative correlation indicates that a parameter increased while the second one decreased and vice-versa.
These provide a large number of both positive and negative correlations between the main parameters of the analysed wines. There are some relevant examples:

Alcohol & Total acidity, (r^2 = 0.615 **); Alcohol & Volatile acidity (r^2 = 0.757**); Alcohol & Non-Reducible extract (r^2 = 0.869**); Alcohol & Coloring intensity (r^2 = 0.876**); Alcohol & Color tint (r^2 = 0.874**); Alcohol & Total polyphenols (r^2 = 0.853**); Alcohol & Anthocyanis (r^2 = 0.862**); Total acidity & Volatile acidity (r^2 = 0.601**); Total acidity & Non-Reducible extract (r^2 = 0.715**); Total acidity & Coloring intensity (r^2 = 0.659**); Total acidity & Color tint (r^2 = 0.611**); Total acidity & Total polyphenols (r^2 = 0.722**); Total acidity & Anthocyanis (r^2 = 0.759**); Volatile acidity & Non-Reducible extract (r^2 = 0.671**); Volatile acidity & Coloring intensity (r^2 = 0.724**); Volatile acidity & Color tint (r^2 = 0.725**); Volatile acidity & Total polyphenols (r^2 = 0.706**); Volatile acidity & Anthocyanis (r^2 = 0.691**); Non-Reducible extract & Sugar content (r^2 = 0.691**); Non-Reducible extract & Coloring intensity (r^2 = 0.877**); Non-Reducible extract & Color tint (r^2 = 0.855**); Non-Reducible extract & Total polyphenols (r^2 = 0.881**); Non-Reducible extract & Anthocyanis (r^2 = 0.917**); Coloring intensity & Color tint (r^2 = 0.996**); Coloring intensity & Total polyphenols (r^2 = 0.944**); Coloring intensity & Anthocyanis (r^2 = 0.948**); Color tint & Total polyphenols (r^2 = 0.926**); Color tint & Anthocyanis (r^2 = 0.930**); Total polyphenols & Anthocyanis (r^2 = 0.952**) (Table 4). Regarding negative correlations it can be observed that in all the analyzed cased there was a weak negative correlation Alcohol & Free SO_2 (r^2 = -0.336*); Volatile acidity & Free SO_2 (r^2 = -0.301*); Volatile acidity & Total SO_2 (r^2 = -0.459*) (Table 4).

Concerning Pearson correlation coefficient between metals from wine (Table 5) there are small number of both positive and negative correlations between the metal concentrations of the analysed wines. There are some relevant examples: K & Na (r^2 = 0.252*); K & Ca (r^2 = -0.411*); K & Li (r^2 = 0.247*); Na & Mg (r^2 = 0.238*); Mg & Fe (r^2 = -0.501**); Fe & Mn (r^2 = -0.407**); Fe & Zn (r^2 = -0.393**); Cu & Zn (r^2 = -0.272*); Mn & Zn (r^2 = 0.250*).

Based on the previous Pearson correlation index, through this present research have been shown that the main parameters analysed from wine have had an influence on each other; in other words, the quality of the wine produced in the Vineyard of Dealu Bujorului is directly contingent on all these parameters.

Combining the physico-chemical characteristics of red wines with elemental concentration for wine geographical discrimination

Multivariate chemometric method was applied for the differentiation of wines intro groups on the basis of their geographic origin. Stepwise linear discriminant analysis (LDA) was used to identify significant tracers for classification to the geographical discrimination of the wines samples. By cross-validation, we established the optimal number of parameters required to obtain a robust model.

Based on the physico-chemical characteristics and elemental concentration the cross-validation technique provided a 75.31% percentage of predicted membership according to the wine geographic origin (F1 = 52.67% and F2 = 22.64%) (Figure 1). A significant differentiation of wines according to physico-chemical characteristics and elemental concentration was carried out for wines samples, which demonstrates the importance of the physico-chemical characteristics and elemental concentration for the geographical traceability of wines.

Table 4. Total metal concentration from wine samples (n = 3) (mg/L)

Area/Vineyard	Variety	Year	K	Na	Ca	Mg	Fe	Cu	Mn	Zn	Li
			Parameters Analyzed								
	Maximum permissible limit		-	**60 mg/L**	-	-	-	**1 mg/L**	-	**5 mg/L**	-
Dealu Bujorului	Sauvignon blanc	2015	127.62±5.72 d	37.65±3.18 c	67.55±1.74 c	107.39±1.67 d	3.49±0.54 a	0.76±0.06 c	0.28±0.05 e	0.92±0.06 f	11.64±0.59 c
		2016	190.59±3.44 cd	40.39±1.63 bc	56.47±3.01 e	105.09±3.53 d	3.58±0.43 a	0.73±0.07 c	0.27±0.02 e	1.03±0.16 e	12.39±1.20 b
	Fetească regală	2015	187.84±4.02 cd	22.41±0.90 d	77.01±5.93 b	108.49±3.47 d	2.23±0.62 b	0.78±0.04 c	0.33±0.02 d	3.16±0.05 b	14.15±0.47 a
		2016	180.58±7.98 cd	42.27±0.37 b	72.40±1.17 b	122.95±0.61 bc	1.43±0.57 f	0.92±0.03 a	0.61±0.09 a	3.06±0.09 b	12.76±0.46 b
	Fetească neagră	2015	328.38±3.01 b	38.27±1.72 c	60.82±2.86 d	122.15±0.75 bc	1.86±0.62 c	0.70±0.06 c	0.17±0.02 f	2.48±0.14 c	14.67±0.35 a
		2016	436.58±4.53 b	51.82±0.98 a	54.95±3.65 e	107.76±4.77 d	1.74±0.10 e	0.63±0.03 cd	0.52±0.15 b	2.46±0.13 c	14.98±1.17 a
	Merlot	2015	485.79±2.14 a	41.55±0.62 b	49.85±1.56 e	127.61±6.08 bc	2.10±0.65 bc	0.73±0.02 c	0.21±0.08 e	2.23±0.08 c	11.64±1.21 c
		2016	489.38±0.21 a	41.95±0.70 b	54.55±3.01 e	122.58±1.10 bc	2.13±0.01 bc	0.65±0.03 cd	0.25±0.06 e	2.20±0.13 c	12.26±1.16 b
Murfatlar	Sauvignon blanc	2015	138.66±6.41 d	37.90±2.78 c	65.88±0.40 c	108.46±3.51 d	2.83±0.16 b	0.76±0.06 c	0.29±0.06 e	1.26±0.05 d	11.38±0.89 c
		2016	154.06±4.06 cd	40.06±1.06 b	61.80±6.06 d	106.09±0.40 d	3.58±0.43 a	0.80±0.04 bc	0.27±0.02 e	0.99±0.01 f	12.72±0.81 b
	Fetească regală	2015	185.60±3.69 cd	46.01±1.32 ab	72.34±1.92 b	106.82±2.91 d	1.96±0.15 d	0.85±0.04 b	0.33±0.02 d	2.13±0.02 c	13.58±1.04 ab
		2016	176.62±2.66 cd	41.60±0.92 b	72.73±2.52 b	125.29±3.82 bc	1.19±0.15 f	0.94±0.03 a	0.61±0.09 a	1.23±0.10 d	12.76±0.46 b
Târnavelor	Sauvignon blanc	2015	153.33±1.67 cd	27.90±2.31 d	56.55±2.60 e	131.73±4.92 b	1.83±0.16 d	0.36±0.05 f	0.46±0.05 c	2.83±0.35 c	11.31±0.98 c
		2016	157.39±2.35 cd	41.72±0.50 b	57.14±2.50 e	144.42±2.71 a	1.58±0.43 e	0.35±0.05 f	0.42±0.11 c	3.25±0.07 b	11.39±1.96 c
	Fetească regală	2015	185.60±3.69 cd	42.34±0.80 b	42.34±1.92 g	111.15±3.27 c	1.37±0.04 f	0.52±0.10 d	0.34±0.07 d	4.01±0.19 a	12.48±0.24 b
		2016	196.62±2.66 cd	42.27±0.37 b	69.40±3.61 c	118.62±4.54 c	1.30±0.17 f	0.36±0.14 f	0.54±0.13 b	2.21±0.10 c	12.42±0.20 b
Iași	Sauvignon blanc	2015	151.99±0.64 cd	27.57±1.74 d	78.22±3.64 a	128.39±6.14 bc	2.49±0.73 b	0.42±0.10 e	0.31±0.10 d	2.15±0.36 c	10.71±1.44 d
		2016	147.39±2.35 cd	43.39±1.63 b	78.47±1.27 a	101.83±3.56 d	2.92±0.96 b	0.43±0.04 e	0.29±0.06 e	1.38±0.13 d	12.05±1.38 b
	Fetească regală	2015	185.60±3.69 cd	24.34±4.16 d	79.01±6.94 a	131.15±6.98 a	2.23±0.62 bc	0.31±0.08 f	0.34±0.07 d	2.25±0.18 c	12.86±0.69 b
		2016	186.62±2.66 cd	40.27±1.38 b	74.73±1.24 b	125.29±3.82 bc	1.43±0.57 e	0.34±0.09 f	0.38±0.08 d	1.84±0.52 d	13.09±1.35 ab
Ștefănești-Argeș	Sauvignon blanc	2015	196.66±6.39 cd	29.57±1.74 d	69.88±3.09 c	126.14±0.51 bc	1.66±0.45 d	0.76±0.06 c	0.33±0.12 d	1.05±0.16 e	13.31±1.02 ab
		2016	177.39±2.35 cd	25.72±5.09 d	48.47±1.27 f	145.29±3.82 a	3.25±0.67 ab	0.53±0.12 d	0.43±0.05 c	1.00±0.02 e	13.31±1.68 ab
	Fetească regală	2015	192.27±2.58 cd	31.34±2.09 c	82.34±1.92 a	136.49±3.74 a	1.44±0.38 e	0.81±0.08 b	0.27±0.06 e	1.11±0.09 e	12.82±2.31 b
		2016	166.62±2.66 cd	42.93±1.45 b	74.17±2.47 b	141.95±8.02 a	1.77±0.56 d	0.81±0.09 b	0.58±0.08 b	2.11±0.05 c	13.09±0.66 b
	Fetească neagră	2015	335.97±7.09 b	37.20±2.13 c	44.82±4.44 e	124.15±4.04 bc	1.86±0.62 d	0.77±0.10 c	0.31±0.11 d	1.07±0.06 e	14.00±0.23 a

Table 4. Continued

Area/Vineyard	Variety	Year	K	Na	Ca	Mg	Fe	Cu	Mn	Zn	Li
			Parameters Analyzed								
	Maximum permissible limit		-	**60 mg/L**	-	-	-	**1 mg/L**	-	**5 mg/L**	-
Argeș		2016	177.39±2.35 cd	25.72±5.09 d	48.47±1.27 f	145.29±3.82 a	3.25±0.67 ab	0.53±0.12 d	0.43±0.05 c	1.00±0.02 e	13.31±1.68 ab
	Fetească regală	2015	192.27±2.58 cd	31.34±2.09 c	82.34±1.92 a	136.49±3.74 a	1.44±0.38 e	0.81±0.08 b	0.27±0.06 e	1.11±0.09 e	12.82±2.31 b
		2016	166.62±2.66 cd	42.93±1.45 b	74.17±2.47 b	141.95±8.02 a	1.77±0.56 d	0.81±0.09 b	0.58±0.08 b	2.11±0.05 c	13.09±0.66 b
	Fetească neagră	2015	335.97±7.09 b	37.20±2.13 c	44.82±4.44 e	124.15±4.04 bc	1.86±0.62 d	0.77±0.10 c	0.31±0.11 d	1.07±0.06 e	14.00±0.23 a
Ștefănești-Argeș		2016	326.70±4.99 b	34.17±4.12 c	66.67±1.07 d	111.12±2.14 c	2.92±1.01 b	0.47±0.03 e	0.31±0.09 d	1.72±0.45 d	13.03±2.53 ab
	Merlot	2015	291.12±5.49 b	25.55±1.49 d	49.18±0.43 e	117.75±3.11 c	2.11±0.32 bc	0.73±0.02 c	0.27±0.13 e	0.73±0.16 g	12.64±0.53 b
		2016	107.75±5.78 d	34.62±4.67 c	53.76±2.14 e	124.92±4.24 bc	1.90±0.69 d	0.63±0.01 d	0.24±0.04 e	1.17±0.11 e	12.92±0.98 b
		Average	265.67	37.37	61.63	119.10	2.13	0.64	0.32	1.85	13.02
F (Fisher Factor)			54.115	4.463	12.091	10.569	6.765	24.396	2.828	17.550	3.850
Sig.			***	***	***	***	***	***	**	***	***
Area		F	5.732	8.291	8.347	7.067	2.418	54.500	1.721	22.326	2.561
		Sig.	***	***	***	***	ns	***	ns	***	*
Variety		F	0.835	28.977	0.090	0.163	0.015	2.495	10.826	3.185	0.092
		Sig.	ns	***	ns	ns	ns	ns	**	ns	ns
Area x Variety		F	0.934	4.361	1.791	3.721	1.191	2.976	1.047	3.121	0.564
		Sig.	ns	ns	ns	**	ns	*	ns	*	ns
dos Santos *et al.*, 2010			1093.00±86.00	-	34.00±5.00	42.00±8.00	2.10±0.40	0.12±0.07	2.00±0.30	1.00±0.50	-
Geana *et al.*, 2014			431.84±209.23	10.50±8.78	26.88±14.08	46.40±25.10	1.22±0.66	0.15±0.07	0.84±0.44	0.56±0.47	0.01±0.0.05
Avram *et al.*, 2014			276.18	60.46	69.40	113.64	-	-	-	-	-
Karataș *et al.*, 2015			387.01±13.41	100.39±9.25	84.41±4.27	45.24±6.29	14.23±3.15	0.97±0.07	1.57±0.38	2.15±0.75	-
Geana *et al.*, 2016			1647.00±111.00	33.50±15.40	11.20±2.90	17.30±4.70	2.40±1.30	1.00±0.20	0.50±0.40	0.36±0.20	0.02±0.04
Đurđić *et al.*, 2017			798	37.05	86.00	118.70	1.42	0.92	0.77	0.37	-

Average value ± standard deviation (n = 3). Romans letters represent the significance of the variety difference ($p \leq 0.05$). The difference between any two values, followed by at least one common letter, is insignificant.

Table 5. Pearson correlation matrix between the main analysed wine parameters

Parameters	Alc.	Tot. A	Vol. A	Non. R. E.	S Cont.	pH	F SO_2	T SO_2	C Int.	C Tint.	T Poly.	Anth.
Alc.	1.000											
Tot. A	0.615**	1.000										
Vol. A	0.757**	0.601**	1.000									
Non. R. E.	0.869**	0.715**	0.671**	1.000								
S Cont.	0.459**	0.519**	0.484**	0.619**	1.000							
pH	0.086	-0.246*	0.091	0.040	-0.076	1.000						
F SO_2	-0.336**	-0.560**	-0.301**	-0.399**	-0.314**	0.298**	1.000					
T SO_2	0.523**	-0.302**	-0.459**	-0.395**	-0.125	0.046	0.325**	1.000				
C Int.	0.876**	0.659**	0.724**	0.877**	0.353**	-0326**	-0.326**	-0413**	1.000			
C Tint.	0.874**	0.611**	0.725**	0.855**	0.325**	-0.305**	-0305**	-0.424**	0.996**	1.000		
T Poly.	0.853**	0.722**	0.706**	0.881**	0.408**	-0.395**	-0.395**	-0.318**	0.944**	0.926**	1.000	
Anth.	0.862**	0.759**	0.691**	0.917**	0.419**	-0.419**	-0.419**	-0.368**	0.948**	0.930**	0.952**	1.000

Alc. = Alcohol (% vol.); Tot. A = Total acidity (g/L $C_4H_8O_6$); Vol. A = Volatile acidity (g/L CH_3COOH); Non. R. E. = Non-Reducible extract (g/L); S Cont. = Sugar content (g/L); F SO_2 = Free SO_2; T SO_2 = Total SO_2; C Int. = Coloring intensity; C Int. = Color tint; T Poly. = Total polyphenols (g/L); Anth. = Anthocyanis (g/L).
*the correlation is significant at $p < 0.05$ in 95%; ** the correlation is highly significant at $p < 0.01$, in 99%; N = 84.

Table 6. Pearson correlation matrix between the main analysed wine parameters

Parameters	K	Na	Ca	Mg	Fe	Cu	Mn	Zn	Li
K	1.000								
Na	0.252*	1.000							
Ca	-0.411**	-0.128	1.000						
Mg	0.011	0.238*	0.044	1.000					
Fe	-0.107	-0.154	-0.052	-0.501**	1.000				
Cu	0.095	0.183	-0.004	-0.124	0.010	1.000			
Mn	-0.189	0.190	0.161	0.176	-0.407**	0.023	1.000		
Zn	0.101	0.160	0.038	0.139	-0.393**	-0.272*	0.250*	1.000	
Li	0.247*	0.134	-0.044	-0.091	-0.127	0.246*	-0.022	0.005	1.000

K = Potassium; Na = Sodium; Ca = Calcium; Mg = Magnesium; Fe = Iron; Cu = Copper; Mn = Manganese; Zn = Zinc; Li = Lithium.
*the correlation is significant at $p < 0.05$ in 95%; ** the correlation is highly significant at $p < 0.01$, in 99%; N = 84.

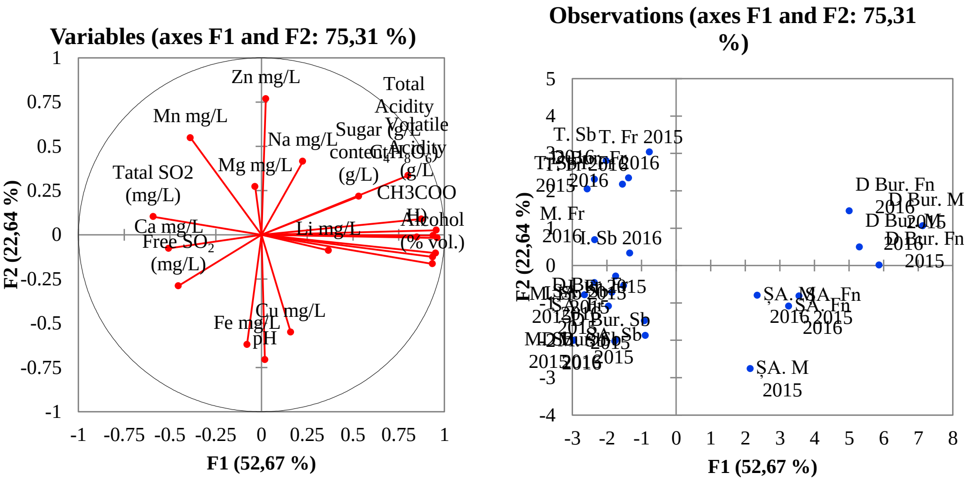

Figure 1. Correlation between physico-chemical characteristics of red wines with elemental concentration and the factors in discriminant analysis of wines geographic origin.

The differentiation of wines according to geographic origin based on the elemental concentration of wine, in this case a 70.63% percentage of predicted membership according to the wine geographic origin (F1 = 39.21% and F2 = 31.44%) (Figure 2). The differentiation of wines according to geographic origin based on the physico-chemical characteristics of red wine, in this case a 85.15% percentage of predicted membership according to the wine geographic origin (F1 = 63.66% and F2 = 21.50%) (Figure 3).

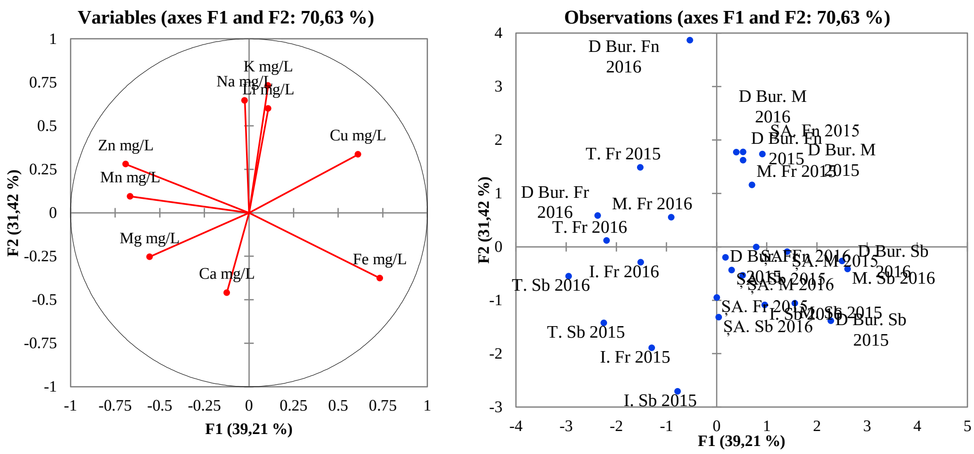

Figure 2. Correlation between elemental concentration and the factors in discriminant analysis of wines geographic origin.

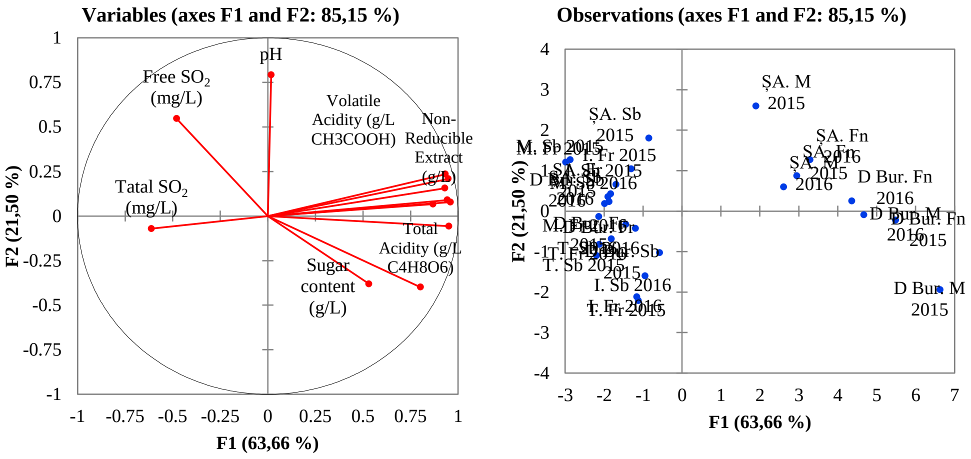

Figure 3. Correlation between physico-chemical characteristics of red wines and the factors in discriminant analysis of wines geographic origin.

Conclusions

Based on the results regarding the qualitative assessment of the tested varieties, they have a very good suitability in the studied areas. In terms of quality rating, they display particular characters of the varieties, as well as the ecoclimatic conditions and ecopedological influence on the quality of wine.

This higher content of some metals may be due to the use of fertilizers for cultivation of vine (K, Ca, Cu) the winemaking process or addition of substances for wine clearing such as bentonite (Na, Ca, Fe) or alos, and the viticultural practices. Cu content is below the limit of detection due to the modern technology for obtaining wines in a controlled manner. The work offers new information on the quality of the white wines obtained in main vineyards of Romania, useful for their promotion and marketing.

Based on the previous Pearson correlation index, through this present research have been shown that the main parameters analysed from wine have had an influence on each other; in other words, the quality of the wine produced in the Vineyard of Dealu Bujorului is directly contingent on all these parameters.

Based on the physico-chemical characteristics and elemental concentration, a relevant discrimination of wines according to their geographical origin and years was performed. The variation of the physico-chemical characteristics and elemental concentration represents a strong geological marker for wines geographical traceability. The proposed methodology allowed an 85.15% successful classification of wines according to the region of provenance and also the years of wine obtaining.

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