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Original Article

# Elemental Profile and $^{207}Pb/^{206}Pb$, $^{208}Pb/^{206}Pb$, $^{204}Pb/^{206}Pb$, $^{87}Sr/^{86}Sr$ Isotope Ratio as Fingerprints for Geographical Traceability of Romanian Wines

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**Abstract**

Geographical wine traceability is an important topic in the context of wine authentification. Therefore, many researchers have addressed this subject by developing different methodologies based on multivariate analysis of organic and inorganic parameters and also by isotopic signature. The goal of this research was to assess the potential of elemental composition and isotopic signature of lead ($^{207}Pb/^{206}Pb$, $^{208}Pb/^{206}Pb$ and $^{204}Pb/^{206}Pb$) and strontium ($^{87}Sr/^{86}Sr$) of wines from three Romanian vineyards, in order to highlight reliable markers for wine geographical origin. The ICP-MS method was used for the concentration determination for 30 elements (Ag, Al, As, Ba, Be, Bi, Ca, Cd, Co, Cr, Cs, Cu, Fe, Ga, In, K, Li, Mg, Mn, Na, Ni, Pb, Rb, Se, Sr, Tl, V, U, Zn, Hg). In this study 10 wines (2 red and 8 white) obtained from 'Merlot', 'Fetească neagră', 'Fetească albă', 'Fetească regală', 'Băbească gri', 'Şarba', 'Aligoté', 'Sauvignon blanc', 'Muscat Ottonel', 'Italian Riesling' cultivars were investigated. The wine samples were obtained from micro-wine production under conditions of 2014, 2015, 2016 from Dealu Bujorului, Murfatlar and Ştefăneşti-Argeş vineyards. The high level of K (148.66±5.41-633.74±4.13 mg/L), Mg (88.23±0.84-131.66±3.42 mg/L), Ca (49.84±1.22-89.18±2.34) and Fe were observed in the wine samples analysed. Heavy metals like Hg, Pb, As and Cd (10.2-315 µg/L) were found below acceptable limits. Concentration of Na (1 mg/L), Cu (1 mg/L), As (0.2 mg/L), Cd (0.01 mg/L), Zn (5 mg/L) and Pb (0.15 mg/L) metals in analysed wine samples were under Maximum Permissible Limits (MPL), respectively as published by the Organization of Vine and Wine. The variation of the $^{207}Pb/^{206}Pb$, $^{208}Pb/^{206}Pb$, $^{204}Pb/^{206}Pb$ and $^{87}Sr/^{86}Sr$ ratio and K/Rb, Ca/Sr of the investigated wine clearly demonstrated that these variables are suitable traces for wine geographical origin determination. The proposed methodology allowed a 100% successful classification of wines according to the region of provenance.

***Keywords:*** geographic origin, isotope ratio, metal composition, wine fingerprint

***Abbreviations:*** GI = Geographical Indications; (LoD) = Limit of Detection; (LoQ) = Limit of Quantification; LDA = Linear Discriminant Analysis; MPL = Maximum Permissible Limits; NISR-SRM: National Institute of Standards and Technology – Standard Reference Material; OIV: The International Organization of Vine and Wine; PPB = Parts per billion; PDO = Protected Designation of Origin

## Introduction

The traceability of foods has become a priority among consumers, driven by the increasing demand for food quality and food safety (Martins *et al.*, 2013). In the traceability system, the discrimination of the geographical provenance of food products is essential to verify the claims of origin of the declared-on labels and to prevent unsafe products from reaching the consumers (Barbaste *et al.*, 2002). The geographical origin assessment of wine is of particular interest, being one of the most important factors that determine its commercial values (Petrini *et al.*, 2015). Consumers are attributing lately more values regarding the certification of food products, their origins and authenticity (Vinciguerra *et al.*, 2015).

To establish the geographical origin of wines is a major concern issue for many countries around the world, in order to protect quality products in the case of false statements

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regarding their geographical origin (Versari *et al*., 2014). This can lead to actions that may have negative economic impact to wine industry (Geana *et al*., 2016).

Determination of the elemental composition of wines is useful for many reasons. Firstly, the concentration of elements in wine is useful information to vine grower and oenologists for controlling the process of obtaining high and quality wines (Pohl, 2007). Secondly, the elemental composition could be used as a wine fingerprint and represents one of the criteria for evaluating the authenticity of wine (Grindlay *et al*., 2008).

The minerals in wine originate from the capacity of the vine to take elements from soil (geographical region), the climatic factors such as heavy rains, environmental conditions (pollution), and also agricultural applications pesticides and fertilizers (Şen and Tokatli, 2014). The mineral content in white and red wines from the same region can differ due to the impact of the vinification process on the elemental composition, such as the maceration step in red winemaking, where the juice is in longer contact whit the skins and flesh of the grapes (Coetzee *et al*., 2005).

Based on these factors, the elements in wine can be classified into two groups: endogenous and exogenous (Grindlay *et al*., 2011). The most abundant are endogenous elements (Ca, Mg, Na, K, Zn, and P) that are related to the grape variety and maturity, type of soil in the vineyard, and ecoclimatic conditions (Đurđić *et al*., 2017). The exogenous elemental content (Al, Cd, Cr, Cu, Fe, and Zn) depends on external impurities during the growth of grapes and vinicultural and winemaking practices (Pohl, 2007; Ivanova-Petropulos *et al*., 2013; Versari *et al*., 2014). Anthropogenic factors, such as application of fungicides, pesticides and fertilisers during the growing season, can lead to an increase in Cd, Cu, Mn, As, and Zn in wine. The presence of Pb in wines can originate from sources like traffic, fertilisers, vessels, and pumps used during vinification process (Almeida and Vasconcelos, 1999). Recent data indicate that some beverages, including wine (red and also white), contribute to the total dietary intake of certain trace elements (B, Ba, Co, Mn, Ni, Rb, Sb, Tl, and V) (Grindlay *et al*., 2011; Tariba *et al*., 2011; Ivanova-Petropulos *et al*., 2016) and iron as well (Đurđić *et al*., 2017).

The most used chemical parameters for discriminating the geographical origin of wine are the stable isotope ration of oxygen, carbon and hydrogen (Dordevic *et al*., 2012; Raco *et al*., 2015; Geana *et al*., 2016) and also the elemental composition (Fabani *et al*., 2010; Selih *et al*., 2014) including rare elements (Gonzálvez *et al*., 2009) and $^{87}Sr/^{86}Sr$ isotope ratio (Durante *et al*., 2013; Marchionni *et al*., 2013; Geana *et al*., 2016) or a combination of them (Dutra *et al*., 2011). The ability to differentiate wines by regions through their elemental patterns suggests that elements are mainly regulated by their migration from rock to soil and from vineyard soil to grapes. Elements are taken up by the roots passing to the grapes in the same isotopic proportions as they occur in the soil (Almeida and Vasconcelos, 2003).

Generally, the elements which are selected as tracers for geographic origin of wines must have a strong correlation between the wine composition and the geochemistry of provenance soil (Vorster *et al*., 2010). The elemental profile of wine may be affected by several factors such as agricultural practices, environmental contamination, climatic change and also the winemaking process, which affects the wine elements content (Almeida and Vasconcelos, 2003).

The control of the geographical origin of wine based on its chemical composition is one of the most challenging issues in relation to wines authenticity. In the last decade, many efforts have been made for identify potential markers and develop reliable analytical methods to determine the wines authenticity (Martins *et al*., 2013). The application of methods using stable isotopes of light elements (H, C, O, S and N) have been started since the beginning of the 1950, providing information on climate, distance from the sea, latitude, altitude and technological practices (Morgun *et al*., 2008; Loftus *et al*., 2016).

More recently, the study of isotopic ratios of heavy metals such Pb and Sr came into use in this field application, providing additional information on the geographical origin, since plants inherit the isotopic signature of these elements from the geological and pedological environmental (Horn *et al*., 1993; Barbaste, 2001; Rummel *et al*., 2010; Martins *et al*., 2013).

Strontium is found in nature as three abundant isotopes: $^{86}Sr$ (9.75-9.99%), $^{87}Sr$ (6.94-7.14%), $^{88}Sr$ (82.29-82.77%) and $^{84}Sr$ (0.55-0.58%) as less abundant isotope (Berglund and Wieser, 2011; Martins *et al*., 2013). The $^{87}Sr$ is radiogenic and therefore the $^{87}Sr$ content increases with time due to radioactive decay of $^{87}Rb$ (Geana *et al*., 2016). Since the content of $^{87}Sr$ in soil varies with geological age and geographical location, the $^{87}Sr/^{86}Sr$ isotopic ratio can be used as a tracer for determining the geographical origin of wine (Vorster *et al*., 2010). Many studies have shown that there is a significant correlation between isotopic ratio $^{87}Sr/^{86}Sr$ from wines and soils of origin (Di Paola-Naranjo *et al*., 2011; Durante *et al*., 2013), thus representing the starting premise for geographical origin determination. The isotopic ration $^{87}Sr/^{86}Sr$ is a well-established tool for dating and tracing the origin of rocks and also minerals (Capo *et al*., 1998) with special interest of wine traceability. Several studies on its use for wine geographical origin assessment can be found in literature (Horn *et al*., 1993; Almeida and Vasconcelos, 2004; Durante *et al*., 2013; Catarino *et al*., 2016). Recently, within a research program regarding strategies for wine fingerprinting, the authors confirmed $^{87}Sr/^{86}Sr$ as a viable tool for traceability of Romanian PDO and GI wines (Geana *et al*., 2016), Portuguese PDO, where soils were developed on different geological formations (Martins *et al*., 2014; Catarino *et al*., 2016). The use of this parameter as a marker of wine geographical origin is based on the assumption that a relation between soil, plants and wine exists. Therefore, $^{87}Sr/^{86}Sr$ ratio should not be significantly modified during wine processing. Aiming to use $^{87}Sr/^{86}Sr$ for traceability and authentication of wine, it is mandatory to clarify the impacts of anthropogenic factors and technological processes on this isotopic ration (Catarino *et al*., 2016).

Lead is found in nature as three abundant isotopes: $^{206}Pb$ (20.84-27.48%), $^{207}Pb$ (17.62-23.65%), $^{208}Pb$ (51.28-

56.21%) and $^{204}Pb$ (1.04-1.65%) as less abundant isotope (Rossman and Taylor, 1998). Their abundance extensively varies because of different decay pathways from $^{238}U$, $^{235}U$ and $^{232}Th$ to $^{206}Pb$, $^{207}Pb$, $^{208}$ Pb respectively (Faure, 1986). The Pb isotope of ore deposits and anthropogenic sources has their distinct isotopic ratios or signatures (Cheng and Hu, 2010). The Pb isotope ratio did not change in industrial or environmental processing and retained its characteristic ratio from source ore (Ault *et al*., 1970). The Pb isotope ratio can be used to identify the sources and transport pathways of Pb in pollution studies (Hu *et al*., 2015). Previous works have shows that the use of lead isotopes is a good tool in order to know the origin of Pb and to identify the types of Pb according to anthropogenic or geogenic origin (Ettler *et al*., 2004; Li *et al*., 2011; Álvarez-Iglesias *et al*., 2012); this is because the Pb emitted into the atmosphere maintains a characteristic isotopic composition (signature) and does not change during the physical/physicochemical processes associated with smelting, refining or manufacturing (Flegal and Smith, 1995). The Pb from anthropic sources has less radiogenic ratios than from geogenic sources (1.21-1.33, $^{206}Pb/^{207}Pb$). Therefore, the sources of Pb pollution heave specific ration that allow them to be differentiated. Many studies have shown that there is a significant correlation between isotope ration $^{206}Pb/^{207}Pb$, $^{208}Pb/^{206}Pb$ from wines and soil of origin (Avram *et al*., 2014; Kristensen *et al*., 2016; Dehelean and Voica, 2012; Almeida *et al*., 2016), this representing the starting premise for geographical origin determination. The lead isotope ratio depends on factors such as thorium and uranium content in the soil, weathering processes and original rock age, which provide a fingerprint used for different forensic and archeological purposes (Komárek *et al*., 2008; Roux *et al*., 2004; Dreyfus *et al*., 2007). Lead isotopic analysis of wines from Bordeaux, France showed that lead from wines changed over time to reflect the dominant source of atmospheric lead pollution in southern France (Médina *et al*., 2000).

The premise from which we started this research is that the elemental profile of wines reflects the chemical composition of vineyard soil (Coetzee *et al*., 2005; van der Linde *et al*., 2010). The aim of the present research is to determine the elemental composition and $^{207}Pb/^{206}Pb$, $^{208}Pb/^{206}Pb$, $^{204}Pb/^{206}Pb$ and $^{87}Sr/^{86}Sr$ isotopic ratio for red and white wines from three different Romanian winemaking regions, in order to highlight reliable markers for wine geographical origin.

## Materials and Methods

### *Study area*

A total of 90 wine samples were analysed (2 red wines and 8 white wines). Samples originated from three different regions in Romania: Dealu Bujorului vineyard (45°52′10″ N, 27°55′8″E) (n = 30), Murfatlar vineyard (44°10′25″ N, 28°24′30″ E) (n = 30) and Ștefănești-Argeș vineyard (44°51′53″ N, 24°57′0″ E) (n = 30). 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 having a clayey sand texture with pH between values 7.4 and 8.1. Although they have moisture deficit, natural conditions (ecoclimatic and ecopedological) offer viable ecosystem for the development of vineyard. The Murfatlar region landscape is characterized by high fragmentation; with altitude between 0 and 100 m and the predominant soil chernozem having clayey sand texture with pH values between 7.6-8.3. 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. The average annual temperature was: 11.6 °C (Dealu Bujorului vineyard), 14.1 °C (Murfatlar vineyard) and 10.1 °C (Ștefănești-Argeș vineyard).

### *Sample collection and microvinification process*

The samples used in this experiment were obtained from the wines produced from 'Merlot', 'Fetească neagră', 'Fetească albă', 'Fetească regală', 'Băbească gri', 'Șarba', 'Aligoté', 'Sauvignon blanc', 'Muscat Ottonel', 'Italian Riesling' under the conditions of 2014, 2015 and 2016 year, from Dealu Bujorului, Murfatlar and Ștefănești-Argeș vineyard. 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 °C before analysis. One bottle was used for each sample, and three replicates were taken. All vines were planted since 1979, and the vine plantation was organized with 2.2 × 1 m distance between rows and plants. Vines were pruned according to the Guyot system and were grown on speliers.

### *Reagents and solutions*

Thirty elements (Ag, Al, As, Ba, Be, Bi, Ca, Cd, Co, Cr, Cs, Cu, Fe, Ga, In, K, Li, Mg, Mn, Na, Ni, Pb, Rb, Se, Sr, Tl, V, U, Zn and Hg) were determined in order to assess their ability to discriminate wines by geographical origin. The analysis was made using multielement analysis and ICP-MS technique, after an appropriate dilution, using external standard calibration method. Each sample was analyzed in duplicate and each analysis was prepared from consisted of three replicates. The calibration was performed using XXICertiPUR multielement standard, and from individual standard solution of Hg. The working standards and the control sample were prepared daily from the intermediate standards that were prepared from the stock solution. The intermediate solutions stored in polyethylene bottles and glassware was cleaned by soaking in 10% v/v $HNO_3$ for 24 hours and rinsing at least ten rimes with ultrapure water (Milli-Q Integral ultrapure water-Type 1). The accuracy of the methods was evaluated by replicate analyses of known concentration samples (between 10 µL to 10 mL concentrations) and the obtained values ranged between 0.8-13.1 percent, depending on the element. The global recovery for each element was estimated and the obtained values were between 84.6-100.9% (Geana *et al*., 2016).

For quality control purpose, blanks and triplicates samples (n = 3) were analyzed during the procedure. The variation coefficient was under 5% and detection limits (ppb) were determined by the calibration curve method.

Limit of detection (LoD) and Limit of quantification (LoQ) limits were calculated according to the next mathematical formulas: LoD = 3SD/s and LoQ = 10 SD/s (SD = estimation of the standard deviation of the regression line; s = slope of the calibration curve).

To verify the achieved accuracy and precision, ten NIST-SRM 987 and NIST-SRM 982 analysis results were pooled together with the calculated relative standard deviation presented in Table 2. Based on the obtained results, it was verified that, applying quadrupole ICP-MS, relative standard deviation and reproducibility of approximately 0.5% for $^{87}Sr/^{86}Sr$, $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$ are feasible. The results were in agreement with those reported by (Ketterer *et al*., 1991; Barbaste *et al*., 2001; Almeida *et al*., 2016; Geana *et al*., 2016).

*Sample preparation for determination of metals and isotope ratio from wine using ICP-MS*

For the determination of metals from wine samples were used an amount of 0.5 mL wine and adjust 8 mL (7 mL $HNO_3$ 65%+1 mL $H_2O_2$), after 15-30 minutes the mineralization was performed using a microwave system Milestone START D Microwave Digestion System set in three steps: step I (time 10 min., temperature 200 °C), step II (time 15 min., temperature 200 °C) and step III (time 60 min., ventilation - temperature 35 °C).

After mineralization, samples were filtered through a 0.45 mm filter and brought to a volume of 50 mL. The Pb and Sr isotope ration in the analysed wine samples ($^{206}Pb/^{207}Pb$, $^{208}Pb/^{206}Pb$, $^{206}Pb/^{204}Pb$, $^{87}Sr/^{86}Sr$,) were determined according to the usual methodology (Mihaljevič *et al*., 2006; Álvarez-Iglesias *et al*., 2012; Voster *et al*., 2010; Geana *et al*., 2016).

*Instrumentation*

The determination of metals was performed on mass spectrometer with inductively coupled plasma (ICP-MS) iCAP Q Thermo scientific model, based polyatomic species before they reach the quadrupole mass spectrometer, using a PFA micro flow concentric nebulizer. The argon used was of 99.99% purity (Messer, Austria). The instrument was daily optimized to give maximum sensitivity for $M^+$ ions and the double ionization and oxides monitored by the means of the ratio between $Ba^{2+}/Ba^+$ and $Ce^{2+}/CeO^+$, respectively, these always being less than 2%. The experimental conditions 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 °C). Accuracy was calculated for the elements taken into consideration (0.5-5.0%).

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

| Element | Correlation coefficient | LoD* (µg/L) | LoQ*** (µg/L) | BEC** (µg/L) | Element | Correlation coefficient | LoD* (µg/L) | LoQ*** (µg/L) | BEC** (µg/L) |
|---|---|---|---|---|---|---|---|---|---|
| Ag | 0.999 | 0.045 | 0.149 | 0.006 | K | 0.999 | 2.186 | 7.279 | 31.728 |
| Al | 0.999 | 0.090 | 0.302 | 5.282 | Li | 0.999 | 0.004 | 0.016 | 0.020 |
| As | 0.999 | 0.233 | 0.777 | 0.538 | Mg | 0.999 | 2.732 | 9.099 | 9.099 |
| Ba | 0.999 | 1.107 | 3.688 | 2.159 | Mn | 0.999 | 0.010 | 0.034 | 0.085 |
| Be | 0.999 | 0.000 | 0.003 | 0.002 | Na | 0.999 | 3.980 | 13.256 | 32.121 |
| Bi | 0.999 | 0.006 | 0.020 | 0.003 | Ni | 0.999 | 0.059 | 0.196 | 0.091 |
| Ca | 0.999 | 5.664 | 18.864 | 20.820 | Pb | 0.999 | 0.000 | 0.001 | 0.002 |
| Cd | 0.999 | 0.020 | 0.067 | 0.027 | Rb | 0.999 | 0.002 | 0.008 | 0.008 |
| Co | 0.999 | 0.036 | 0.121 | 0.152 | Se | 0.999 | 0.501 | 1.669 | 0.920 |
| Cr | 0.999 | 1.663 | 5.537 | 0.636 | Sr | 0.999 | 0.143 | 0.477 | 0.955 |
| Cs | 0.999 | 0.000 | 0.000 | 0.001 | Tl | 0.999 | 0.002 | 0.006 | 0.002 |
| Cu | 0.999 | 0.040 | 0.133 | 0.237 | V | 0.999 | 1.214 | 4.042 | 4.263 |
| Fe | 0.999 | 5.210 | 17.350 | 71.399 | U | 0.999 | 0.025 | 0.084 | 0.005 |
| Ga | 0.999 | 0.010 | 0.035 | 0.042 | Zn | 0.999 | 0.378 | 1.258 | 5.401 |
| In | 0.999 | 0.003 | 0.010 | 0.009 | Hg | 0.999 | 0.041 | 0.137 | 0.128 |

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

Table 2. Strontium isotopic ration and Lead isotopic ration determination precision and accuracy based on the NIST SRM 987 (Strontium) and NIST SRM (Lead) 982 (n = 10)

| Replicate | $^{207}Pb/^{206}Pb$ (b) | RSD (%) | $^{208}Pb/^{206}Pb$ (c) | RSD (%) | $^{204}Pb/^{206}Pb$ (d) | RSD (%) | $^{87}Sr/^{86}Sr$ (a) | RSD (%) |
|---|---|---|---|---|---|---|---|---|
| 1 | 0.46483 | 0.51 | 0.99891 | 0.67 | 0.00271 | 0.32 | 0.70493 | 0.31 |
| 2 | 0.47891 | 0.48 | 0.99452 | 0.61 | 0.00272 | 0.41 | 0.72046 | 0.45 |
| 3 | 0.46978 | 0.32 | 0.99794 | 0.55 | 0.00275 | 0.28 | 0.70325 | 0.63 |
| 4 | 0.47123 | 0.64 | 0.99688 | 0.64 | 0.00273 | 0.51 | 0.70634 | 0.48 |
| 5 | 0.46987 | 0.56 | 0.99726 | 0.48 | 0.00246 | 0.14 | 0.71478 | 0.36 |
| 6 | 0.46154 | 0.37 | 0.99647 | 0.56 | 0.00258 | 0.39 | 0.71245 | 0.59 |
| 7 | 0.47362 | 0.70 | 0.99969 | 0.34 | 0.00279 | 0.47 | 0.70987 | 0.46 |
| 8 | 0.45641 | 0.43 | 0.99744 | 0.58 | 0.00278 | 0.51 | 0.72326 | 0.42 |
| 9 | 0.41562 | 0.36 | 0.99576 | 0.59 | 0.00273 | 0.49 | 0.70845 | 0.68 |
| 10 | 0.45612 | 0.45 | 0.99874 | 0.61 | 0.00278 | 0.36 | 0.10789 | 0.47 |
| Average | 0.46179 | 0.48 | 0.99736 | 0.56 | 0.00270 | 0.41 | 0.71117 | 0.49 |

[a]Certified value = $^{207}Pb/^{206}Pb$, $^{208}Pb/^{206}Pb$, $^{204}Pb/^{206}Pb$ and $^{87}Sr/^{86}Sr$ (0.71034±0.00026); [b]Certified value = $^{207}Pb/^{206}Pb$ (0.46707±0.00020);[c]Certified value = $^{208}Pb/^{206}Pb$ (1.00016±0.00036); [d]Certified value = $^{204}Pb/^{206}Pb$ (0.027219±0.00027); RSD (%) = relative standard deviation.

*Statistical analysis*

The statistical interpretation of the results was performed using the Duncan test, SPSS Version 24 (SPSS Inc., Chicago, IL., USA). The statistical processing of the results was primarily performed in order to calculate the following statistical parameters: average and standard deviation. This data was interpreted with the analysis of variance (ANOVA) and the average separation was performed with the DUNCAN test at $p \leq 0.005$. 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**

*Wine mineral content*

These elements are present in grapes as results of their accumulation in the vine plant through the root from the soil, or they could originate from the agents used in protecting the vine from diseases. During the maceration, extracted elements are absorbed at the cell membrane of yeast, and afterward, their declines as a result of precipitation together with the yeast cell or precipitation in complexation reactions.

The elemental contents of the investigated wines according to the geographical origin are present in Appendix 1, 2, 3 as mean and standard deviation. 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). According to our results, the K concentration was higher in red compared to white wines. The measured values ranged between 491.12±4.49 to 633.74±4.13 mg/L for red wines and from 148.66±5.41 to 327.64±9.00 mg/L for white wines (Appendix 3).

These results agree with 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). Magnesium and calcium were the second abundant elements in our study. The magnesium concentration was higher in red wines (mean 100.67 mg/L, values between 99.91±1.35 to 129.28±5.64) than in white wine (mean 93.76 mg/L, values between 88.23±0.84 to 131.66±3.42), while calcium concentration were similar in both types of wines (62.56 mg/L and 69.60 mg/L for red and white wines, respectively). 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).

The same as Mg concentration, the average content of Na differed among the regions and decreased in the order Dealu Bujorului > Ştefăneşti-Argeş > Murfatlar. The highest concentration of Na (55.59±1.11 mg/L Şarba (2014)) was found in wines Dealu Bujorului. The sodium concentration was higher in red wines (mean 44.74 mg/L, values between 36.89±0.30 to 51.62±0.64) than in white wines (mean 42.08 mg/L, values between 31.35±1.25 to 55.59±1.11). These results are in agree with Ražić and Onjia (2010) where they obtained the similar concentration of sodium in wine from North Serbia (33±11 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 higher content of sodium in Dealu Bujorului and Murfatlar wines has been attributed to the vicinity of the Black Sea.

Li, Cu, Fe, Mn, Co and V 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). The average values obtained for V were 557.89 μg/L and 525.05 μg/L in red and white wines, respectively. The results indicated that Romanian wines are moderately rich in vanadium, and the results obtained are similar with Macedonian (Ivanova-Petropulos *et al.*, 2013), Spanish (Iglesias *et al.*, 2007) and Czech (Kment *et al.*, 2005) wines and have more vanadium than Belgian (Coetzee *et al.*, 2014) ones. Regarding concentration of Li, Cu and Mn the highest concentration were obtained in red wines (mean 12.63 mg/L (Li) values between 0.40±0.05 to 14.69±0.40 to 11.37±1.22; mean 0.68 mg/L (Cu) values between 0.40±0.05 to 0.85±0.07; mean 0.53 mg/L (Mn) values between 0.21±0.02 to 0.83±0.16) than in white wines (mean 12.31 mg/L (Li) values between 9.44±0.91 to 15.63±0.53; mean 0.63 mg/L (Cu) values between 0.24±0.06 to 0.91±0.04; mean 0.50 mg/L (Mn) values between 0.14±0.02 to 0.97±0.02). While the highest concentration of Fe and Co were obtained at white wines (mean 3.07 mg/L (Fe) values between 1.09±0.03 to 4.86±0.21; mean 5.38 mg/L (Co) values between 3.27±0.33 to 7.77±0.53) (Appendix 1).

The content of trace elements (In, Sr, Ni, Rb, Se, Tl, U, Zn, Ag, Al, Be, Bi, Ba, Cr, Cs and Ga) found in Romanian wines agreed with literature data (Kment *et al.*, 2005; Filket *et al.*, 2011; Ivanova-Petropulos *et al.*, 2013; Geana *et al.*, 2013). Regarding Ni, Rb, Se, Tl, U, Ag, Cr and Cs the highest concentration were obtained at red wines, and in the case of In, Sr, Zn, Al, Be, Bi and Ba the highest concentration were obtained at white wines. The results indicated that Romanian red wines are moderately rich in In, Sr, Ni, Rb, Se, Tl, U, Zn, Ag, Al, Be, Bi, Ba, Cr, Cs and Ga while white wines are moderately rich In, Sr, Zn, Al, Be, Bi and Ba (Appendix 2-3).

Regarding the content of toxic elements (Hg, Pb, As and Cd) found in Romanian wines agreed with literature data (Avram *et al.*, 2014; Đurđić *et al.*, 2017). The As content was higher than in published data (Kment *et al.*, 2005; Lara *et al*., 2005; Iglesias *et al*., 2007; Filket *et al*., 2011; Alkiş *et al*., 2014), while the Pb content was lower than that in Czech (Kment *et al*., 2005) and Romanian wines (Geana *et al*., 2013) (Appendix 2-3).

In general Area, Variety, Years, Area × Variety, Area × Years, Variety × Years and Area × Variety × Years factors influenced accumulation of Ca, Mg, Fe, V, Ag, Al, Bi, Ba, Cr, Cs, In, Sr, Ni, Rb, Se, Tl, U, Zn, Hg and Pb.

Concerning the influence factors on the accumulation of metals in wines, it can be seen that in case of Ca, Mg, Fe, V, Ag, Al, Bi, Ba, Cr, Cs, In, Sr, Ni, Rb, Se, Tl, U, Zn, Hg and Pb was significantly influenced by Area, Variety, Years, Area × Variety, Area × Years, Variety × Years and Area x Variety x Years factors and in case of K, Li, Cu, Na, Mn, Co, As Be, Cd and Ga was significantly influenced distinctive by the factors taken into consideration.

Concentration of Na (1 mg/L), Cu (1 mg/L), As (0.2 mg/L), Cd (0.01 mg/L), Zn (5 mg/L) and Pb (0.15 mg/L) metals in analysed wine samples were under Maximum Permissible Limits (MPL), respectively as published by the Organization of Vine and Wine (OIV 2016).

*$^{206}Pb/^{207}Pb$, $^{208}Pb/^{206}Pb$, $^{206}Pb/^{204}Pb$, $^{87}Sr/^{86}Sr$, isotope ratio and ratio of K/Rb, Ca/Sr from wine samples*

The $^{206}$Pb/$^{207}$Pb and $^{206}$Pb/$^{208}$Pb ratios are commonly used as tracers to differentiate natural and anthropogenic lead. In Central Europe, the lead isotopic ratio, as signatures of pollution sources, ranges from relatively high $^{206}$Pb/$^{207}$Pb ratios (natural Pb, coals, fly ashes, $^{206}$Pb/$^{207}$Pb=1.1700-1.2200) to low $^{206}$Pb/$^{207}$Pb values (gasoline, petrol combustion, $^{206}$Pb/$^{207}$Pb = 1.0600-1.1400) (Mihaljevič *et al*., 2003; Avram *et al*., 2014).

Regarding $^{206}$Pb/$^{207}$Pb isotope ratios based on analyses it can be concluded that the vines grown in the Dealu Bujorului (1.1374±0.0011 [0.0957]) and Murfatlar (1.1046±0.0024 [0.2174]) areas, the values of isotopic ratio of these varieties of vine traces of pollution comes from cars (automobile emissions) (if $^{206}$Pb/$^{207}$Pb=1.1000-1.1400 [automobile emissions]). While $^{206}$Pb/$^{207}$Pb isotope ratio from Ştefăneşti-Argeş area shows traces of atmospheric pollution with lead on vine (if $^{206}$Pb/$^{207}$Pb=1.1700-1.2200 [atmospheric pollution]) (Table 3). The values of $^{206}$Pb/$^{207}$Pb isotope ratio are between the ranges from 1.1028 to 1.1781, values comparable with Avram *et al.* (2014) (1.1100 to 1.2000 Romania wines) and Almeida *et al.* (2016) (1.1440 to 1.1820 Brazilian wines). The abundance of the lead isotopes $^{204}$Pb (non-radiogenic), $^{206}$Pb, $^{207}$Pb and $^{208}$Pb (radiogenic) originated from the genesis of the substrate and does not varies with geological ages. The original composition of soil samples retains its chemical composition from the geographical area it belongs to (Shirahata *et al*., 1980; Gulson *et al*., 1981; Elbaz-Poulichet *et al*., 1984). This property is useful in order to identify of the source of lead in a subjected wine sample provided that the measurements of the isotope ratio is precise and accurate.

The values of $^{208}$Pb/$^{206}$Pb and $^{204}$Pb/$^{206}$Pb isotope ratio are between the ranges from 2.0386 to 2.1191 ($^{208}$Pb/$^{206}$Pb) and 16.5727 to 18.0647 ($^{204}$Pb/$^{206}$Pb). The highest values of $^{208}$Pb/$^{206}$Pb were registered to vine varieties grown in Dealu Bujorului (2.1064±0.0034 [0.1627]) followed by vine varieties grown in Ştefăneşti-Argeş area (2.0493±0.0051 [0.3114]). Regarding $^{204}$Pb/$^{206}$Pb isotope ratio the highest values were registered to vine varieties grown in Murfatlar area (18.0389±0.0160 [0.0886]) and Ştefăneşti-Argeş area (17.0388±0.0374 [0.2199]), while the vine varieties grown in Dealu Bujorului was recorded the lowest isotope ratio (16.9692±0.0329 [0.1981]). The values of $^{208}$Pb/$^{206}$Pb and $^{206}$Pb/$^{204}$Pb isotope ratio obtained are comparable with Almeida *et al.* (2016) (2.0700 to 2.1570 Brazilian wines $^{208}$Pb/$^{206}$Pb; 16.6670 to 17.9960 Brazilian wines $^{204}$Pb/$^{206}$Pb) and also with Barbaste *et al*., 2001 (2.0990 to 2.1030 Italian wines $^{208}$Pb/$^{206}$Pb; 17.544 to 18.3210 Italian wines $^{204}$Pb/$^{206}$Pb).

Concerning $^{87}$Sr/$^{86}$Sr, isotope ratio the values are between the ranges from 0.7023 to 0.7681, the highest values were registered to vine varieties grown in Ştefăneşti-Argeş (0.7649±0.0026 [0.3438]) and Dealu Bujorului area (0.7170±0.0048 [0.6683]), lowest value of $^{87}$Sr/$^{86}$Sr isotope ratio was Murfatlar area (0.7058±0.0046 [0.6516]) (Table 3). The values of $^{87}$Sr/$^{86}$Sr isotope ratio obtained are comparable with Geana *et al.* (2016) (0.71015 to 0.72311 Romanian wines); Avram *et al*., (2014) (0.7600 to 0.9300). Lower $^{87}$Sr/$^{86}$Sr isotope ratio of wine from Murfatlar area is due to influence of saline aerosols, with a $^{87}$Sr/$^{86}$Sr isotope ratio of about 0.70917 (Rodrigues *et al*., 2011; Geana *et al*., 2016).

The ratio of different metals (K/Rb and Ca/Sr) are important due to the fact that the K/Rb ratio can differ significantly between different roks and soil and the Ca/Sr ration is used as a chemical tracer in the biochemistry and hydro-geochemistry studies (Di Paola-Naranjo *et al*., 2011; Geana *et al*., 2016). Concerning the element ratio, wine from the Ştefăneşti-Argeş area (898.89±4.21) have higher K/Rb ration, those from the Dealu Bujorului (675.44±4.53) shows higher K/Rb ratio. Wine from the Murfatlar area shows lower Ca/Sr ratio (21.09±1.08) and wine from Dealu Bujorului shows lower Ca/Sr ratio (14.83±0.98) (Table 3).

Variation of the $^{206}$Pb/$^{207}$Pb, $^{208}$Pb/$^{206}$Pb, $^{206}$Pb/$^{204}$Pb, $^{87}$Sr/$^{86}$Sr, isotope ratio and ratio of K/Rb, Ca/Sr in wines with different geographical origins confirm the link with geological substratum of the production territory, making the $^{206}$Pb/$^{207}$Pb, $^{208}$Pb/$^{206}$Pb, $^{206}$Pb/$^{204}$Pb, $^{87}$Sr/$^{86}$Sr, isotope ration and ratio of K/Rb, Ca/Sr a robust instrument for tracing the geographical provenance of wines.

*Combining multielemental analysis and $^{207}Pb/^{206}Pb$, $^{208}Pb/^{206}Pb$, $^{204}Pb/^{206}Pb$, $^{87}Sr/^{86}Sr$, isotope ratio for wine geographical discrimination*

Elements like Mn, Cd, Li, Ba, Ca, Bi, Rb, Mg, Ag, Ni, Cr, Sr, Zn, Rb, Pb and Fe showed a high discriminatory power for geographic origin of Romanian, but additional new elements (Hg, Ag, As, Al, Tl, U), metal ratio (K/Rb and Ca/Sr), and $^{207}$Pb/$^{206}$Pb, $^{208}$Pb/$^{206}$Pb, $^{204}$Pb/$^{206}$Pb, $^{87}$Sr/$^{86}$Sr isotope ratio have been investigate in order to indentify new tracers for geographical traceability of Romanian wines.

In this study, the content of certain wines shows high concentration of metals, but not exceeding the maximum recommended by International Organisation of Vine and Wine (OIV 2016), and this mostly due to agricultural practices, fertilizers and technological winemaking processes. Thus, Ca and other elements like Cu, K, which are affected by exogenous factors, were not considered for wines geographical discrimination (Geana *et al*., 2016).

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 elemental contents and metal ratio (K/Rb and Ca/Sr) data, the cross-validation technique provided a 100 % percentage of predicted membership according to the wine geographic origin (F1 = 65.28% and F2 = 34.72%) (Fig.1). The linear correction revealed acceptable scores for the two defined discriminant factors (F1 and F2). A significant differentiation of wines according to the geographic origin was carried out for wines, which demonstrates the importance of elemental profile for the geographical traceability of wines.

Table 3. $^{206}Pb/^{207}Pb$, $^{208}Pb/^{206}Pb$, $^{204}Pb/^{206}Pb$, $^{87}Sr/^{86}Sr$, isotope ratio and ratio of K/Rb, Ca/Sr from wine samples

| Areas | Variety | Year | $^{207}Pb/^{206}Pb$ ± SD (RSD %) | $^{208}Pb/^{206}Pb$ ± SD (RSD %) | $^{204}Pb/^{206}Pb$ ± SD (RSD %) | $^{87}Sr/^{86}Sr$ ± SD (RSD %) | K/Rb | Ca/Sr |
|---|---|---|---|---|---|---|---|---|
| Dealu Bujorului | 'Merlot' | 2014 | 1.1350±0.0010 (0.0811) | 2.1054±0.0039 (0.1843) | 16.6663±0.0307 (0.1645) | 0.7151±0.0016 (0.2187) | 770.45±1.96 | 11.77±0.42 |
| | | 2015 | 1.1350±0.0002 (0.0183) | 2.1044±0.0040 (0.1918) | 16.6167±0.0102 (0.0615) | 0.7189±0.0058 (0.8113) | 728.52±3.83 | 13.11±1.02 |
| | | 2016 | 1.1337±0.0017 (0.1457) | 2.1069±0.0057 (0.2704) | 16.6640±0.0173 (0.1039) | 0.7260±0.0217 (2.9903) | 664.90±9.65 | 15.92±0.55 |
| | 'Fetească neagră' | 2014 | 1.1358±0.0025 (0.2175) | 2.1040±0.0040 (0.2086) | 16.6473±0.0438 (0.2629) | 0.7158±0.0057 (0.7896) | 638.72±3.03 | 12.06±1.30 |
| | | 2015 | 1.1378±0.0001 (0.0051) | 2.1069±0.0054 (0.2578) | 16.6383±0.0174 (0.1045) | 0.7175±0.0067 (0.9352) | 720.67±2.23 | 11.86±0.27 |
| | | 2016 | 1.1347±0.0021 (0.1809) | 2.1095±0.0062 (0.2941) | 16.6477±0.0399 (0.2395) | 0.7178±0.0019 (0.2654) | 720.05±1.35 | 15.93±2.36 |
| | 'Fetească albă' | 2014 | 1.1371±0.0020 (0.1241) | 2.1023±0.0027 (0.1263) | 16.6543±0.0295 (0.1771) | 0.7166±0.0086 (1.1953) | 705.29±4.45 | 12.36±1.21 |
| | | 2015 | 1.1324±0.0015 (0.1352) | 2.1089±0.0029 (0.1382) | 16.6397±0.0439 (0.2637) | 0.7176±0.0035 (0.4853) | 702.27±3.07 | 14.12±0.76 |
| | | 2016 | 1.1329±0.0006 (0.0486) | 2.1091±0.0041 (0.1936) | 16.6363±0.0383 (0.2301) | 0.7182±0.0055 (0.0055) | 721.06±1.34 | 15.48±1.07 |
| | 'Fetească regală' | 2014 | 1.1358±0.0006 (0.0536) | 2.1063±0.0023 (0.1087) | 16.6363±0.0459 (0.2758) | 0.7182±0.0054 (0.0054) | 467.26±2.16 | 13.01±1.68 |
| | | 2015 | 1.1339±0.0026 (0.2266) | 2.1104±0.0017 (0.0817) | 16.6663±0.0302 (0.1814) | 0.7162±0.0076 (1.0606) | 525.75±5.01 | 13.95±0.89 |
| | | 2016 | 1.1349±0.0019 (0.1666) | 2.1079±0.0069 (0.3271) | 16.6643±0.0341 (0.2044) | 0.7197±0.0045 (0.6252) | 480.72±1.86 | 12.78±0.41 |
| | 'Băbească gri' | 2014 | 1.1359±0.0006 (0.0485) | 2.1041±0.0015 (0.0713) | 16.6230±0.0274 (0.1649) | 0.7179±0.0068 (0.9536) | 664.98±8.78 | 13.88±1.40 |
| | | 2015 | 1.1369±0.0009 (0.0746) | 2.1076±0.0035 (0.1677) | 16.6407±0.0427 (0.2567) | 0.7146±0.0037 (0.5171) | 630.86±2.06 | 15.47±1.05 |
| | | 2016 | 1.1345±0.0008 (0.0700) | 2.1047±0.0018 (0.0852) | 16.6447±0.0395 (0.2373) | 0.7172±0.0038 (0.5249) | 676.38±6.61 | 15.15±1.55 |
| | 'Şarba' | 2014 | 1.1257±0.0003 (0.0235) | 2.1078±0.0029 (0.1363) | 16.6483±0.0353 (0.2123) | 0.7161±0.0062 (0.8645) | 841.99±6.79 | 16.05±0.53 |
| | | 2015 | 1.1307±0.0005 (0.0468) | 2.1065±0.0052 (0.2483) | 16.6537±0.0271 (0.1625) | 0.7220±0.0062 (0.8336) | 828.89±6.35 | 17.75±1.28 |
| | | 2016 | 1.1325±0.0012 (0.1046) | 2.1113±0.0081 (0.3848) | 16.6583±0.0489 (0.2932) | 0.7187±0.0060 (0.8329) | 787.49±5.48 | 17.89±2.89 |
| | 'Aligoté' | 2014 | 1.1345±0.0004 (0.0334) | 2.1048±0.0041 (0.1965) | 16.6580±0.0292 (0.1753) | 0.7158±0.0058 (0.8065) | 846.82±6.27 | 9.71±0.52 |
| | | 2015 | 1.1373±0.0005 (0.0416) | 2.1061±0.0054 (0.2549) | 16.6477±0.0399 (0.2395) | 0.7185±0.0062 (0.8581) | 731.15±1.46 | 12.76±1.61 |
| | | 2016 | 1.1335±0.0021 (0.1822) | 2.1080±0.0045 (0.2138) | 16.6313±0.0457 (0.2748) | 0.7183±0.0064 (0.8842) | 657.80±2.86 | 14.19±0.96 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 'Sauvignon blanc' | 2014 | 1.1358±0.0031 (0.2696) | 2.1059±0.0029 (0.1359) | 16.6590±0.0382 (0.2294) | 0.7135±0.0018 (0.7825) | 761.69±7.20 | 15.12±1.34 |
| | | 2015 | 1.1344±0.0020 (0.1770) | 2.1078±0.0064 (0.3031) | 16.6453±0.0435 (0.2613) | 0.7139±0.0014 (0.1912) | 682.09±7.04 | 14.11±0.14 |
| | | 2016 | 1.1329±0.0008 (0.0663) | 2.1048±0.0014 (0.6558) | 16.6420±0.0429 (0.2577) | 0.7154±0.0031 (0.4343) | 650.68±0.97 | 15.37±0.89 |
| | 'Muscat Ottonel' | 2014 | 1.1392±0.0001 (0.0088) | 2.1039±0.0042 (0.1986) | 16.6313±0.0287 (0.1724) | 0.7135±0.0018 (0.2508) | 682.76±7.60 | 19.09±0.60 |
| | | 2015 | 1.1379±0.0010 (0.0880) | 2.1120±0.0040 (0.1897) | 16.5727±0.1603 (0.9670) | 0.7175±0.0070 (0.9693) | 525.87±5.26 | 14.64±0.84 |
| | | 2016 | 1.1329±0.0021 (0.1852) | 2.1086±0.0051 (0.2437) | 16.6493±0.0422 (0.2534) | 0.7195±0.0053 (0.7302) | 701.09±1.36 | 16.84±2.59 |
| | 'Italian Riesling' | 2014 | 1.1390±0.0004 (0.0317) | 2.1041±0.0015 (0.0713) | 16.4457±0.1553 (0.9444) | 0.7222±0.0030 (0.4161) | 519.62±6.57 | 17.63±0.50 |
| | | 2015 | 1.1397±0.0007 (0.0608) | 2.1084±0.0025 (0.1206) | 16.6603±0.0263 (0.1579) | 0.7190±0.0065 (0.9047) | 622.58±9.55 | 15.54±2.71 |
| | | 2016 | 1.1336±0.0019 (0.1681) | 2.1069±0.0073 (0.3446) | 16.6553±0.0299 (0.1794) | 0.7189±0.0057 (0.7869) | 593.82±4.18 | 16.65±1.35 |
| Average | | | **1.1374±0.0011 (0.0957)** | **2.1064±0.0034 (0.1627)** | **16.9692±0.0329 (0.1981)** | **0.7170±0.0048 (0.6683)** | **675.44±4.53** | **14.83±0.98** |
| Murfatlar | 'Merlot' | 2014 | 1.1046±0.0024 (0.2195) | 2.0961±0.0052 (0.2471) | 18.0473±0.0166 (0.0921) | 0.7070±0.0067 (0.9410) | 939.73±7.88 | 21.06±1.41 |
| | | 2015 | 1.1056±0.0030 (0.2677) | 2.0964±0.0052 (0.2461) | 18.0613±0.0346 (0.1918) | 0.7067±0.0034 (0.4770) | 923.72±6.65 | 21.69±0.75 |
| | | 2016 | 1.1050±0.0042 (0.3789) | 2.0966±0.0048 (0.2282) | 18.0237±0.0102 (0.0567) | 0.7042±0.0041 (0.5853) | 926.88±5.11 | 19.67±1.40 |
| | 'Fetească neagră' | 2014 | 1.1054±0.0027 (0.2448) | 2.0980±0.0082 (0.3927) | 18.0333±0.0166 (0.0922) | 0.7079±0.0022 (0.3176) | 912.46±2.16 | 20.95±1.75 |
| | | 2015 | 1.1047±0.0013 (0.1150) | 2.0982±0.0016 (0.1124) | 18.0473±0.0166 (0.0921) | 0.7151±0.0176 (2.4609) | 881.15±2.96 | 20.21±0.96 |
| | | 2016 | 1.1058±0.0029 (0.2615) | 2.0929±0.0052 (0.2502) | 18.0203±0.0159 (0.0885) | 0.7040±0.0039 (0.5584) | 918.56±6.08 | 20.78±0.98 |
| | 'Fetească albă' | 2014 | 1.1031±0.0002 (0.0209) | 2.1000±0.0023 (0.1076) | 18.0350±0.0125 (0.0693) | 0.7050±0.0037 (0.5280) | 931.19±1.50 | 22.34±0.90 |
| | | 2015 | 1.1077±0.0012 (0.1085) | 2.0986±0.0002 (0.0073) | 18.0150±0.0154 (0.0855) | 0.7023±0.0007 (0.0997) | 950.01±2.11 | 19.62±0.96 |
| | | 2016 | 1.1038±0.0041 (0.3721) | 2.0896±0.0012 (0.0595) | 18.0320±0.0115 (0.0640) | 0.7040±0.0042 (0.6028) | 922.42±8.39 | 18.82±0.73 |
| | 'Fetească regală' | 2014 | 1.1031±0.0007 (0.0668) | 2.0958±0.0025 (0.1173) | 18.0477±0.0319 (0.1770) | 0.7026±0.0016 (0.2318) | 836.46±4.41 | 16.62±2.05 |
| | | 2015 | 1.1047±0.0032 (0.2918) | 2.0986±0.0021 (0.0979) | 18.0200±0.0165 (0.0917) | 0.7067±0.0046 (0.6498) | 826.05±4.99 | 18.59±1.05 |
| | | 2016 | 1.1040±0.0043 (0.3923) | 2.0943±0.0050 (0.2371) | 18.0300±0.0017 (0.0096) | 0.7043±0.0036 (0.5179) | 844.48±7.35 | 23.69±1.17 |
| | 'Băbească gri' | 2014 | 1.1036±0.0019 (0.1726) | 2.1002±0.0026 (0.1225) | 18.0510±0.0373 (0.2065) | 0.7086±0.0040 (0.5654) | 929.12±4.87 | 19.29±0.56 |
| | | 2015 | 1.1033±0.0023 (0.2053) | 2.1026±0.0066 (0.1358) | 18.0287±0.0144 (0.0797) | 0.7056±0.0038 (0.5350) | 889.72±4.88 | 18.39±0.86 |
| | | 2016 | 1.1047±0.0036 (0.3293) | 2.0969±0.0015 (0.0708) | 18.0623±0.0348 (0.1929) | 0.7050±0.0037 (0.5280) | 833.25±2.43 | 24.12±3.87 |
| | 'Șarba' | 2014 | 1.1072±0.0016 (0.1429) | 2.0985±0.0041 (0.1930) | 18.0577±0.0326 (0.1805) | 0.7120±0.0072 (1.0134) | 861.81±3.18 | 18.57±1.68 |
| | | 2015 | 1.1028±0.0023 (0.2045) | 2.0999±0.0001 (0.0048) | 18.0203±0.0169 (0.0936) | 0.7030±0.0025 (0.3614) | 787.48±5.48 | 23.29±0.90 |
| | | 2016 | 1.1040±0.0039 (0.3562) | 2.0927±0.0056 (0.2653) | 18.0363±0.0081 (0.0448) | 0.7025±0.0017 (0.2466) | 818.03±6.52 | 21.96±0.63 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 'Aligoté' | 2014 | 1.1090±0.0008 (0.0716) | 2.0973±0.0036 (0.0036) | 18.0647±0.0309 (0.1712) | 0.7027±0.0023 (0.3308) | 785.09±3.92 | 22.33±0.89 |
| | | 2015 | 1.1044±0.0041 (0.3695) | 2.0935±0.0046 (0.2183) | 18.0603±0.0307 (0.1698) | 0.7061±0.0082 (1.1654) | 782.69±1.33 | 21.55±2.61 |
| | | 2016 | 1.1036±0.0019 (0.1758) | 2.0932±0.0058 (0.2758) | 18.0483±0.0165 (0.0914) | 0.7039±0.0044 (0.6197) | 764.27±1.78 | 19.89±1.37 |
| | 'Sauvignon blanc' | 2014 | 1.1035±0.0009 (0.0805) | 2.0974±0.0057 (0.2700) | 18.0387±0.0083 (0.0462) | 0.7067±0.0033 (0.4736) | 926.12±4.92 | 22.35±0.96 |
| | | 2015 | 1.1047±0.0037 (0.3319) | 2.1032±0.0078 (0.3693) | 18.0113±0.0100 (0.0556) | 0.7051±0.0056 (0.7956) | 838.83±2.87 | 22.92±1.42 |
| | | 2016 | 1.1047±0.0042 (0.3757) | 2.0918±0.0032 (0.1546) | 18.0417±0.0095 (0.0524) | 0.7029±0.0025 (0.3532) | 909.84±1.04 | 21.76±0.52 |
| | 'Muscat Ottonel' | 2014 | 1.1046±0.0037 (0.3345) | 2.0748±0.0372 (1.7924) | 18.0480±0.0358 (0.1983) | 0.7077±0.0064 (0.8983) | 910.84±2.04 | 22.07±0.66 |
| | | 2015 | 1.1061±0.0048 (0.4332) | 2.0985±0.0018 (0.0865) | 18.0257±0.0068 (0.0378) | 0.7049±0.0042 (0.5979) | 729.35±1.66 | 24.46±1.04 |
| | | 2016 | 1.1045±0.0038 (0.3424) | 2.0987±0.0002 (0.0095) | 18.0300±0.0155 (0.0861) | 0.7045±0.0012 (0.1735) | 820.59±3.59 | 21.15±1.43 |
| | 'Italian Riesling' | 2014 | 1.1079±0.0010 (0.0904) | 2.0964±0.0051 (0.2413) | 18.0460±0.0155 (0.0860) | 0.7035±0.0020 (0.2839) | 874.85±3.27 | 23.45±2.71 |
| | | 2015 | 1.1043±0.0040 (0.3616) | 2.0966±0.0045 (0.2137) | 18.0227±0.0193 (0.1074) | 0.7055±0.0042 (0.5900) | 728.13±3.37 | 19.89±1.46 |
| | | 2016 | 1.1036±0.1596 (0.1596) | 2.0919±0.0034 (0.1627) | 18.0353±0.0299 (0.1660) | 0.7046±0.0038 (0.5328) | 759.97±9.55 | 21.72±0.55 |
| | Average | | **1.1046±0.0024 (0.2174)** | **2.1028±0.0092 (0.3828)** | **18.0389±0.0160 (0.0886)** | **0.7058±0.0046 (0.6516)** | **857.83±3.62** | **21.09±1.08** |
| Ştefăneşti-Argeş | 'Merlot' | 2014 | 1.1751±0.0033 (0.2801) | 2.0434±0.0070 (0.3405) | 17.0740±0.0218 (0.1206) | 0.7644±0.0017 (0.2190) | 927.59±3.59 | 17.99±0.67 |
| | | 2015 | 1.1734±0.0017 (0.1479) | 2.0496±0.0060 (0.2916) | 17.0580±0.0353 (0.2072) | 0.7632±0.0017 (0.2217) | 920.91±2.08 | 21.14±1.35 |
| | | 2016 | 1.1739±0.0029 (0.2459) | 2.0479±0.0077 (0.3745) | 17.0287±0.0240 (0.1410) | 0.7642±0.0015 (0.1964) | 928.06±3.66 | 21.07±1.34 |
| | 'Fetească neagră' | 2014 | 1.1778±0.0017 (0.1403) | 2.0457±0.0012 (0.0579) | 17.0330±0.0139 (0.0814) | 0.7645±0.0023 (0.3059) | 936.82±5.66 | 22.39±0.91 |
| | | 2015 | 1.1739±0.0016 (0.1348) | 2.0493±0.0062 (0.3043) | 17.0477±0.0444 (0.2605) | 0.7641±0.0024 (0.3169) | 941.24±1.47 | 24.08±2.52 |
| | | 2016 | 1.1766±0.0017 (0.1472) | 2.0504±0.0066 (0.3204) | 17.1043±0.0021 (0.0122) | 0.7611±0.0012 (0.1577) | 857.25±3.61 | 24.08±2.51 |
| | 'Fetească albă' | 2014 | 1.1758±0.0037 (0.3128) | 2.0504±0.0055 (0.2685) | 17.0493±0.0058 (0.0339) | 0.7654±0.0004 (0.0495) | 874.15±6.38 | 20.28±1.11 |
| | | 2015 | 1.1726±0.0020 (0.1663) | 2.0530±0.0056 (0.2868) | 17.0330±0.0221 (0.1296) | 0.7616±0.0002 (0.0227) | 837.92±4.74 | 18.48±0.88 |
| | | 2016 | 1.1736±0.0018 (0.1501) | 2.0488±0.0073 (0.3563) | 17.0830±0.0159 (0.0929) | 0.7636±0.0013 (0.1739) | 850.20±1.92 | 21.17±1.40 |
| | 'Fetească regală' | 2014 | 1.1750±0.0034 (0.2900) | 2.0495±0.0043 (0.2091) | 17.0370±0.0327 (0.1922) | 0.7674±0.0017 (0.2257) | 968.69±3.01 | 20.69±0.98 |
| | | 2015 | 1.1733±0.0002 (0.0148) | 2.0452±0.0061 (0.2968) | 17.0990±0.0089 (0.0520) | 0.7630±0.0025 (0.3222) | 963.46±3.89 | 20.29±0.96 |
| | | 2016 | 1.1764±0.0023 (0.1913) | 2.0476±0.0034 (0.1636) | 17.0510±0.0242 (0.1422) | 0.7634±0.0021 (0.2798) | 934.05±6.29 | 20.38±0.81 |
| | 'Băbească gri' | 2014 | 1.1721±0.0013 (0.1148) | 2.0580±0.0101 (0.4918) | 17.0960±0.0564 (0.3299) | 0.7655±0.0002 (0.0302) | 837.92±4.74 | 21.83±0.46 |
| | | 2015 | 1.1738±0.0010 (0.0874) | 2.0500±0.0058 (0.2812) | 17.1003±0.0040 (0.0236) | 0.7618±0.0006 (0.0758) | 835.56±5.20 | 23.15±2.13 |
| | | 2016 | 1.1734±0.0048 (0.4084) | 2.0486±0.0029 (0.1420) | 17.0813±0.0225 (0.1317) | 0.7656±0.0040 (0.5251) | 848.85±3.27 | 21.03±0.63 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 'Şarba' | 2014 | 1.1749±0.0040 (0.3405) | 2.0386±0.0060 (0.2573) | 17.0313±0.0231 (0.1712) | 0.7649±0.0035 (0.4546) | 953.46±1.91 | 22.05±1.31 |
| | 2015 | 1.1750±0.0013 (0.1130) | 2.0476±0.0039 (0.1892) | 16.7160±0.5430 (3.2486) | 0.7681±0.0023 (0.2929) | 964.74±5.18 | 19.81±1.36 |
| | 2016 | 1.1781±0.0023 (0.1910) | 2.0499±0.0058 (0.2841) | 17.0397±0.0456 (0.2677) | 0.7643±0.0040 (0.5253) | 928.46±6.01 | 18.16±0.61 |
| 'Aligoté' | 2014 | 1.1773±0.0015 (0.1257) | 2.0538±0.0069 (0.3368) | 17.0523±0.0386 (0.2265) | 0.7667±0.0027 (0.3539) | 863.35±6.23 | 19.89±1.53 |
| | 2015 | 1.1770±0.0025 (0.2109) | 2.0512±0.0055 (0.2659) | 17.0727±0.0223 (0.1306) | 0.7673±0.0020 (0.2562) | 852.04±2.88 | 23.39±2.16 |
| | 2016 | 1.1749±0.0040 (0.3405) | 2.0537±0.0071 (0.3452) | 17.0700±0.0242 (0.1421) | 0.7637±0.0020 (0.2574) | 868.38±6.32 | 22.37±0.93 |
| 'Sauvignon blanc' | 2014 | 1.1741±0.0029 (0.2437) | 2.0499±0.0037 (0.3818) | 17.0933±0.0348 (0.2039) | 0.7666±0.0025 (0.3292) | 875.79±4.97 | 25.18±4.17 |
| | 2015 | 1.1736±0.0026 (0.2254) | 2.0492±0.0063 (0.3085) | 17.0553±0.0167 (0.0982) | 0.7633±0.0023 (0.2948) | 911.84±3.05 | 24.71±1.54 |
| | 2016 | 1.1734±0.0047 (0.4035) | 2.0503±0.0056 (0.2726) | 17.0450±0.0389 (0.2284) | 0.7646±0.0037 (0.4832) | 912.22±3.50 | 22.38±1.17 |
| 'Muscat Ottonel' | 2014 | 1.1744±0.0008 (0.0639) | 2.0511±0.0055 (0.0931) | 17.0750±0.0428 (0.2506) | 0.7635±0.0044 (0.2818) | 873.13±1.91 | 15.25±3.51 |
| | 2015 | 1.1742±0.0020 (0.1691) | 2.0467±0.0019 (0.3140) | 17.0530±0.0066 (0.0385) | 0.7653±0.0037 (0.4840) | 902.41±2.85 | 16.25±1.55 |
| | 2016 | 1.1725±0.0029 (0.2487) | 2.0540±0.0044 (0.2136) | 17.1097±0.0693 (0.4048) | 0.7664±0.0017 (0.2269) | 892.83±1.55 | 19.82±1.36 |
| 'Italian Riesling' | 2014 | 1.1731±0.0019 (0.1656) | 2.0486±0.0052 (0.2536) | 17.0545±0.0400 (0.2346) | 0.7644±0.0025 (0.3248) | 912.19±1.55 | 16.51±2.05 |
| | 2015 | 1.1763±0.0023 (0.1947) | 2.0476±0.0035 (0.1692) | 17.0613±0.0254 (0.1490) | 0.7632±0.0017 (0.2170) | 907.29±1.52 | 22.35±1.94 |
| | 2016 | 1.1745±0.0015 (0.1292) | 2.0499±0.0048 (0.2345) | 17.1187±0.0563 (0.3289) | 0.7638±0.0034 (0.4460) | 900.74±0.95 | 20.80±1.01 |
| Average | | **1.1750±0.0024 (0.2044)** | **2.0493±0.0051 (0.3114)** | **17.0388±0.0374 (0.2199)** | **0.7649±0.0026 (0.3438)** | **898.89±4.21** | **20.91±1.26** |

SD - standard deviation, RSD % - relative standard deviation.

Combining the elemental profile and metal ratio with $^{207}Pb/^{206}Pb$, $^{208}Pb/^{206}Pb$, $^{204}Pb/^{206}Pb$, $^{87}Sr/^{86}Sr$, isotope ratio for wine geographical discrimination, a 100% percentage of predicted membership according to the wine geographic origin was obtained (F1 = 78.51% and F2 = 21.49%) (Fig. 2).

Wines were grouped in there distinct groups corresponding to regions of provenance. Moreover, the first discriminant function separated mainly the wines from Murfatlar and Dealu Bujorului from Ştefăneşti-Argeş area and the second one discriminated mainly the wines from Murfatlar from Dealu Bujorului and Ştefăneşti-Argeş area.

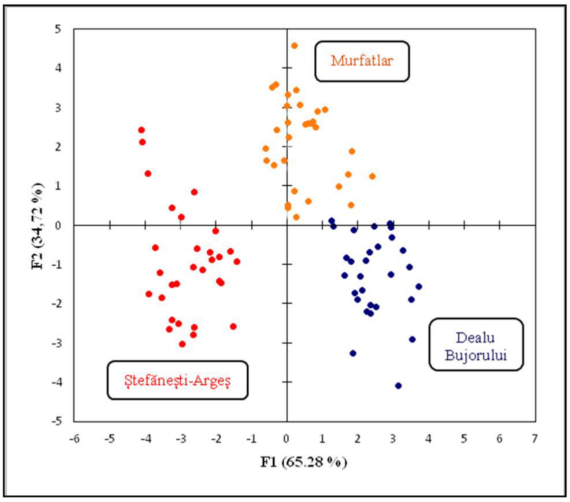


Fig. 1. Differentiation of wines according to geographic origin based on element contents and K/Rb and Ca/Sr ratios

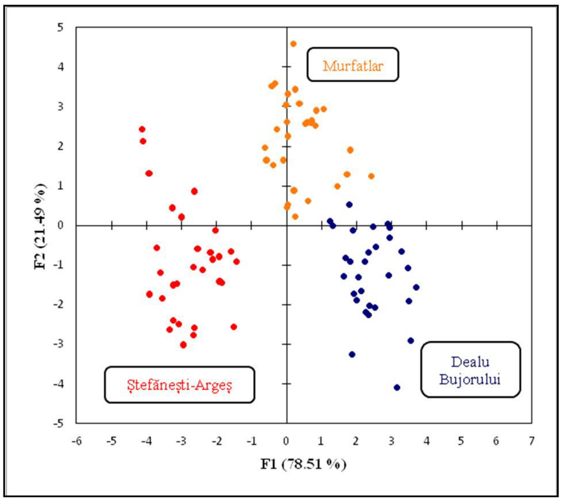


Fig. 2. Differentiation of wines according to geographic origin based on element contents and K/Rb, Ca/Sr ratios and $^{207}Pb/^{206}Pb$, $^{208}Pb/^{206}Pb$, $^{204}Pb/^{206}Pb$, $^{87}Sr/^{86}Sr$

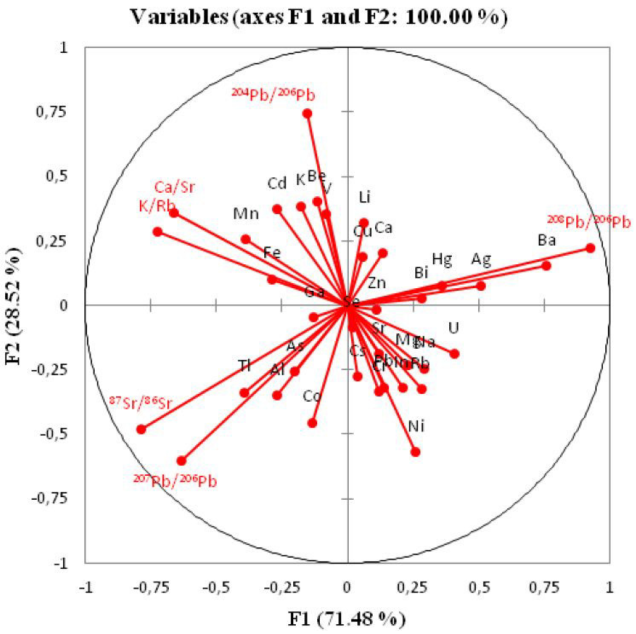


Fig. 3. Correlation between analyzed parameters and the factors in discriminant analysis of wines geographic origin

Among the investigated parameters, Hg, Ag, Al, Tl, U and K/Rb, Ca/Sr ratios and also $^{207}Pb/^{206}Pb$, $^{208}Pb/^{206}Pb$, $^{204}Pb/^{206}Pb$, $^{87}Sr/^{86}Sr$ were identified as the most significant for geographic differentiation of the wine (Fig. 3).

Relevant results for wine geographical classification were achieved, in both cases, with or without the $^{207}Pb/^{206}Pb$, $^{208}Pb/^{206}Pb$, $^{204}Pb/^{206}Pb$, $^{87}Sr/^{86}Sr$ isotope ratio variable, which means that lead and strontium isotope analysis is not imperative for discrimination of wines according to their geographic origin, elemental profile and certain metal ratios being sufficient for this purpose. The technique of cross-validation was applied during the set validation and the proposed model appears to be a promising chemometric approach for precise classification of wines according to their geographical origin. Thus, in both cases, the geographical regions were correctly classified with percentage between 52 and 71 %.

## Conclusions

In this study the characterisation of Romanian wines according to their elemental composition was performed. Potassium, calcium and magnesium were the most abundant elements in all investigated wine samples. Concentration of Na (1 mg/L), Cu (1 mg/L), As (0.2 mg/L), Cd (0.01 mg/L), Zn (5 mg/L) and Pb (0.15 mg/L) metals in analysed wine samples were under Maximum Permissible Limits (MPL), respectively as published by the Organization of Vine and Wine. Based on the elemental profile, the K/Rb and Ca/Sr metal ratio and $^{207}Pb/^{206}Pb$, $^{208}Pb/^{206}Pb$, $^{204}Pb/^{206}Pb$, $^{87}Sr/^{86}Sr$ isotope ratio, a relevant discrimination of wines according to their geographical origin was performed. The variation of $^{207}Pb/^{206}Pb$, $^{208}Pb/^{206}Pb$, $^{204}Pb/^{206}Pb$, $^{87}Sr/^{86}Sr$ isotope ratio represent a strong geological marker for wines geographical traceability. The proposed methodology allowed a 100% successful classification of wines according to the region of provenance.

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Appendix 1. Total metal concentration from wine samples

| Area | Variety | Year | Total metal concentration | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Ca (mg/L) | Mg (mg/L) | K(mg/L) | Na (mg/L) | Li (mg/L) | Cu (mg/L) | Fe (mg/L) | Mn (mg/L) | Co (µg/L) | V (µg/L) |
| | | | M.A.L. | M.A.L. | M.A.L. | M.A.L. | M.A.L. | M.A.L. | M.A.L. | M.A.L. | M.A.L. | M.A.L. |
| | | | - | - | - | 60 mg/L | - | 1 mg/L | - | - | - | - |
| Dealu Bujorului | 'Merlot' | 2014 | 50.18±2.14 | 129.28±5.64 | 491.12±4.49 | 45.55±1.49 | 11.98±0.63 | 0.69±0.04 | 1.77±0.09 | 0.21±0.08 | 4.23±2.07 | 364.69±9.21 |
| | | 2015 | 53.55±2.00 | 121.58±2.00 | 507.75±5.78 | 50.84±1.77 | 11.92±0.76 | 0.62±0.03 | 2.12±0.03 | 0.21±0.02 | 5.10±0.11 | 418.29±4.13 |
| | | 2016 | 51.72±0.53 | 124.49±1.15 | 501.16±1.50 | 51.62±0.64 | 12.36±0.91 | 0.60±0.05 | 3.61±0.06 | 0.48±0.15 | 5.83±0.33 | 451.51±4.68 |
| | 'Fetească neagră' | 2014 | 61.49±1.89 | 117.44±8.72 | 435.97±7.78 | 39.20±2.15 | 14.33±0.93 | 0.73±0.12 | 2.19±0.05 | 0.17±0.01 | 3.41±0.69 | 241.70±5.92 |
| | | 2015 | 56.67±1.07 | 107.79±7.91 | 426.70±4.99 | 41.29±1.35 | 14.69±0.40 | 0.54±0.10 | 1.92±0.06 | 0.24±0.07 | 4.19±0.06 | 246.63±7.02 |
| | | 2016 | 58.59±0.98 | 118.87±2.91 | 429.55±2.05 | 46.59±1.16 | 12.82±0.39 | 0.83±0.05 | 4.25±0.07 | 0.18±0.05 | 4.29±0.77 | 213.22±2.48 |
| | 'Fetească albă' | 2014 | 64.81±3.36 | 102.45±5.17 | 228.80±3.95 | 52.29±1.00 | 9.70±0.59 | 0.51±0.03 | 1.73±0.13 | 0.35±0.17 | 5.86±0.40 | 466.37±10.35 |
| | | 2015 | 66.63±1.63 | 99.55±2.49 | 294.12±6.40 | 49.56±1.94 | 10.95±1.19 | 0.74±0.10 | 1.09±0.03 | 0.47±0.08 | 5.59±1.09 | 516.07±3.60 |
| | | 2016 | 64.59±2.61 | 102.76±3.93 | 259.68±8.79 | 47.63±1.00 | 12.22±0.28 | 0.50±0.05 | 2.59±0.22 | 0.27±0.05 | 4.16±0.01 | 484.65±7.28 |
| | 'Fetească regală' | 2014 | 75.67±5.09 | 107.82±4.37 | 182.27±2.58 | 47.68±1.68 | 14.48±0.79 | 0.88±0.07 | 1.90±0.04 | 0.30±0.02 | 6.37±0.38 | 502.88±6.50 |
| | | 2015 | 74.06±2.38 | 121.95±2.07 | 176.62±7.53 | 41.27±1.48 | 13.42±1.15 | 0.91±0.04 | 1.10±0.02 | 0.68±0.03 | 7.25±0.35 | 429.84±6.20 |
| | | 2016 | 76.32±1.76 | 119.71±1.50 | 197.08±2.50 | 38.48±2.41 | 13.25±0.74 | 0.82±0.06 | 2.53±0.14 | 0.36±0.14 | 5.37±0.37 | 464.33±7.36 |
| | 'Băbească gri' | 2014 | 79.13±2.63 | 99.33±2.68 | 236.26±5.38 | 39.91±1.89 | 12.29±1.00 | 0.37±0.03 | 3.21±0.07 | 0.47±0.08 | 4.30±0.23 | 482.50±9.95 |
| | | 2015 | 79.64±3.94 | 88.86±3.96 | 193.22±5.56 | 35.61±1.03 | 13.38±0.88 | 0.56±0.10 | 2.78±0.21 | 0.43±0.07 | 4.66±0.21 | 527.37±4.55 |
| | | 2016 | 77.85±1.12 | 97.66±1.41 | 244.79±7.31 | 37.31±0.79 | 13.80±0.47 | 0.68±0.05 | 5.62±0.15 | 0.47±0.08 | 5.24±0.36 | 511.68±1.18 |
| | 'Şarba' | 2014 | 58.31±2.62 | 126.42±5.26 | 275.79±6.23 | 55.59±1.11 | 11.66±1.48 | 0.25±0.02 | 2.25±0.10 | 0.14±0.02 | 6.55±0.53 | 729.57±6.99 |
| | | 2015 | 60.61±1.92 | 130.75±2.10 | 200.76±1.97 | 51.08±1.37 | 11.39±1.18 | 0.47±0.10 | 2.54±0.35 | 0.20±0.02 | 6.83±0.44 | 709.49±2.72 |
| | | 2016 | 61.15±1.22 | 131.66±3.42 | 215.95±2.50 | 49.87±1.26 | 9.91±0.30 | 0.65±0.09 | 2.04±0.08 | 0.33±0.01 | 5.66±0.48 | 700.48±2.75 |
| | 'Aligoté' | 2014 | 73.12±1.60 | 110.73±1.40 | 295.44±6.56 | 29.26±1.85 | 15.63±0.53 | 0.54±0.14 | 1.96±0.06 | 0.74±0.17 | 4.33±0.28 | 499.98±3.51 |
| | | 2015 | 77.55±1.44 | 116.00±3.62 | 295.18±10.85 | 33.65±1.73 | 13.39±1.11 | 0.66±0.08 | 2.65±0.09 | 0.59±0.05 | 4.95±0.28 | 511.71±2.31 |
| | | 2016 | 76.33±1.12 | 122.09±3.92 | 289.06±2.12 | 49.22±1.18 | 13.06±0.62 | 0.54±0.08 | 3.58±0.06 | 0.68±0.06 | 5.05±0.19 | 475.10±5.42 |
| | 'Sauvignon blanc' | 2014 | 69.22±2.75 | 103.06±5.84 | 148.66±5.41 | 39.57±1.00 | 11.98±0.63 | 0.82±0.06 | 3.16±0.43 | 0.26±0.05 | 7.16±0.25 | 642.39±9.87 |
| | | 2015 | 58.47±1.27 | 104.22±2.71 | 150.72±3.80 | 41.06±1.32 | 12.39±1.20 | 0.76±0.11 | 3.92±0.24 | 0.26±0.01 | 6.70±0.22 | 591.85±6.70 |
| | | 2016 | 71.23±1.45 | 108.67±2.08 | 158.58±3.30 | 52.42±3.00 | 10.57±0.64 | 0.65±0.08 | 2.55±0.34 | 0.35±0.03 | 7.63±0.80 | 611.98±1.60 |
| | 'Muscat Ottonel' | 2014 | 80.66±1.05 | 127.51±8.19 | 327.64±9.00 | 42.50±1.38 | 9.44±0.91 | 0.51±0.03 | 3.92±0.56 | 0.55±0.11 | 3.46±0.45 | 400.29±1.92 |
| | | 2015 | 78.59±0.84 | 128.45±1.25 | 326.83±9.21 | 41.09±1.36 | 10.53±0.39 | 0.48±0.03 | 2.62±0.24 | 0.52±0.03 | 3.50±0.55 | 560.66±4.24 |
| | | 2016 | 81.09±1.56 | 124.20±0.48 | 312.43±5.51 | 42.38±2.87 | 12.35±1.03 | 0.66±0.06 | 4.41±0.16 | 0.55±0.06 | 4.30±0.22 | 559.24±4.47 |
| | 'Italian Riesling' | 2014 | 67.52±2.01 | 101.09±2.19 | 213.33±1.64 | 55.30±0.89 | 11.29±1.05 | 0.63±0.13 | 1.84±0.10 | 0.91±0.08 | 7.70±0.68 | 507.79±5.05 |
| | | 2015 | 63.32±4.94 | 101.15±2.55 | 200.39±1.30 | 49.85±1.34 | 9.59±0.69 | 0.80±0.04 | 2.19±0.06 | 0.49±0.14 | 6.50±0.58 | 552.40±9.06 |
| | | 2016 | 59.60±1.67 | 99.41±2.57 | 247.75±3.62 | 53.71±2.48 | 12.76±0.46 | 0.70±0.01 | 3.76±0.10 | 0.73±0.16 | 6.09±0.19 | 531.15±4.28 |
| Murfatlar | 'Merlot' | 2014 | 44.79±4.53 | 101.44±2.61 | 621.59±2.38 | 46.70±2.66 | 12.42±1.20 | 0.77±0.08 | 2.49±0.15 | 0.65±0.09 | 2.82±0.23 | 653.22±5.51 |
| | | 2015 | 57.39±5.34 | 99.91±1.35 | 620.20±4.24 | 42.86±1.52 | 11.41±1.03 | 0.71±0.06 | 1.35±0.10 | 0.62±0.11 | 3.35±0.26 | 659.24±2.08 |
| | | 2016 | 51.44±1.78 | 101.05±2.25 | 633.74±4.13 | 47.03±1.29 | 11.37±1.22 | 0.56±0.08 | 3.63±0.04 | 0.75±0.09 | 3.27±0.33 | 643.99±6.36 |
| | 'Fetească neagră' | 2014 | 64.58±2.93 | 100.04±2.01 | 535.25±4.97 | 47.14±1.49 | 13.52±0.55 | 0.40±0.05 | 4.50±0.10 | 0.37±0.09 | 4.19±0.06 | 743.27±3.56 |
| | | 2015 | 49.84±1.22 | 117.42±2.63 | 546.19±5.05 | 40.59±3.44 | 12.87±1.53 | 0.72±0.05 | 3.55±0.07 | 0.74±0.13 | 3.92±0.24 | 697.26±6.78 |
| | | 2016 | 73.76±1.70 | 115.04±2.57 | 521.49±2.05 | 47.34±2.19 | 13.13±0.10 | 0.84±0.07 | 1.39±0.15 | 0.45±0.27 | 3.97±0.25 | 562.90±12.53 |
| | 'Fetească albă' | 2014 | 78.34±3.47 | 99.86±1.61 | 323.26±3.25 | 41.46±2.15 | 11.27±1.08 | 0.80±0.04 | 1.42±0.21 | 0.46±0.09 | 5.65±0.56 | 624.97±3.06 |
| | | 2015 | 85.15±4.22 | 88.23±0.84 | 295.79±5.51 | 40.60±0.91 | 11.38±1.21 | 0.66±0.10 | 2.57±0.09 | 0.28±0.05 | 6.96±0.60 | 679.01±2.81 |
| | | 2016 | 80.99±1.52 | 94.27±1.05 | 307.30±1.97 | 55.45±2.38 | 12.54±0.35 | 0.38±0.03 | 3.68±0.10 | 0.66±0.12 | 5.71±0.57 | 653.33±3.06 |
| | 'Fetească regală' | 2014 | 79.74±6.34 | 121.05±1.62 | 235.86±10.25 | 51.16±1.24 | 13.51±1.10 | 0.55±0.09 | 1.49±0.14 | 0.16±0.03 | 4.40±0.34 | 708.86±3.96 |
| | | 2015 | 70.97±7.94 | 129.71±1.40 | 208.95±2.06 | 48.39±1.07 | 11.62±0.64 | 0.77±0.04 | 3.28±0.24 | 0.33±0.19 | 3.74±0.24 | 682.80±5.86 |
| | | 2016 | 66.08±2.40 | 128.69±3.79 | 234.06±7.36 | 49.15±2.33 | 12.71±0.49 | 0.41±0.02 | 4.86±0.21 | 0.55±0.10 | 4.43±0.41 | 701.52±2.05 |
| | 'Băbească gri' | 2014 | 68.44±0.80 | 107.75±2.90 | 190.95±3.15 | 28.57±3.54 | 12.29±1.00 | 0.60±0.10 | 4.53±0.30 | 0.68±0.06 | 2.60±0.40 | 526.37±4.25 |
| | | 2015 | 55.61±4.38 | 108.52±1.98 | 202.46±6.75 | 31.44±1.04 | 13.43±1.10 | 0.78±0.01 | 4.46±0.11 | 0.67±0.12 | 5.05±0.82 | 595.14±5.82 |
| | | 2016 | 63.66±3.32 | 98.88±0.45 | 216.69±2.58 | 36.98±2.30 | 12.32±0.86 | 0.51±0.04 | 2.91±0.56 | 0.31±0.04 | 4.31±0.23 | 539.49±2.34 |
| | 'Şarba' | 2014 | 89.15±2.58 | 112.08±2.65 | 220.63±2.67 | 39.79±1.41 | 11.59±1.18 | 0.68±0.05 | 3.46±0.19 | 0.52±0.16 | 5.23±0.34 | 621.90±4.84 |
| | | 2015 | 62.23±376 | 114.48±2.68 | 194.02±5.83 | 37.25±1.17 | 12.76±0.46 | 0.91±0.03 | 1.99±0.09 | 0.34±0.10 | 3.66±0.50 | 419.56±6.16 |
| | | 2016 | 77.34±1.12 | 113.98±0.93 | 210.28±5.75 | 38.42±1.10 | 12.07±1.37 | 0.78±0.10 | 1.37±0.15 | 0.66±0.12 | 5.14±1.02 | 558.34±7.67 |
| | 'Aligoté' | 2014 | 49.75±1.57 | 100.13±1.98 | 237.54±3.23 | 38.12±2.86 | 14.13±0.75 | 0.91±0.04 | 3.53±0.11 | 0.35±0.27 | 4.29±0.23 | 356.56±5.89 |
| | | 2015 | 58.68±8.84 | 104.36±4.26 | 259.87±3.66 | 39.30±2.04 | 13.23±0.88 | 0.77±0.07 | 4.48±0.11 | 0.38±0.15 | 7.00±0.44 | 568.18±9.35 |
| | | 2016 | 55.87±1.57 | 101.51±0.75 | 208.17±2.22 | 39.60±0.64 | 14.03±0.44 | 0.90±0.05 | 3.53±0.22 | 0.21±0.02 | 5.96±0.73 | 451.95±4.60 |
| | 'Sauvignon blanc' | 2014 | 85.55±3.72 | 111.09±1.36 | 180.04±4.33 | 41.16±1.46 | 14.00±0.63 | 0.29±0.04 | 2.49±0.15 | 0.80±0.12 | 6.32±0.17 | 621.74±1.87 |
| | | 2015 | 84.14±2.72 | 111.61±0.65 | 209.51±2.29 | 40.52±1.65 | 13.33±2.01 | 0.46±0.11 | 2.01±0.13 | 0.79±0.14 | 3.72±0.26 | 612.96±1.03 |
| | | 2016 | 88.97±1.60 | 117.42±4.63 | 202.61±2.75 | 43.07±0.98 | 13.12±1.12 | 0.73±0.06 | 3.71±0.16 | 0.62±0.06 | 5.90±0.18 | 592.91±5.40 |
| | 'Muscat Ottonel' | 2014 | 68.35±2.66 | 101.09±1.36 | 300.28±2.12 | 39.36±2.07 | 13.26±0.40 | 0.67±0.10 | 4.47±0.16 | 0.35±0.15 | 4.42±0.61 | 464.05±6.29 |
| | | 2015 | 63.40±2.06 | 100.15±1.96 | 291.86±2.57 | 45.02±3.50 | 10.86±1.30 | 0.37±0.04 | 3.49±0.19 | 0.54±0.13 | 5.14±1.32 | 482.74±5.38 |
| | | 2016 | 70.80±1.84 | 99.01±0.85 | 325.37±6.06 | 39.80±1.39 | 12.55±0.37 | 0.72±0.05 | 1.69±0.25 | 0.71±0.08 | 5.24±0.10 | 599.54±1.35 |
| | 'Italian Riesling' | 2014 | 39.37±3.22 | 111.19±1.52 | 220.91±3.14 | 46.78±2.82 | 11.35±1.07 | 0.51±0.04 | 2.41±0.24 | 0.47±0.14 | 4.69±0.46 | 522.48±2.47 |
| | | 2015 | 47.76±7.74 | 106.62±2.55 | 241.26±1.48 | 43.87±1.68 | 12.76±0.46 | 0.78±0.10 | 3.54±0.05 | 0.51±0.16 | 5.10±0.10 | 555.81±5.70 |
| | | 2016 | 40.76±4.17 | 107.60±2.59 | 200.00±1.38 | 42.19±0.95 | 14.04±1.36 | 0.83±0.06 | 2.52±0.15 | 0.21±0.02 | 5.73±0.68 | 511.49±4.23 |
| Ştefăneşti-Argeş | 'Merlot' | 2014 | 77.57±1.31 | 110.30±5.23 | 609.04±4.08 | 45.47±4.14 | 14.05±1.37 | 0.85±0.06 | 3.49±0.21 | 0.76±0.09 | 5.53±0.99 | 540.86±7.04 |
| | | 2015 | 69.84±1.30 | 107.59±1.88 | 578.49±13.19 | 49.28±1.85 | 11.28±1.07 | 0.79±0.02 | 2.51±0.17 | 0.68±0.05 | 6.49±0.43 | 609.99±3.54 |
| | | 2016 | 73.74±3.67 | 108.43±0.39 | 593.71±6.48 | 50.72±0.93 | 12.35±0.81 | 0.58±0.03 | 3.39±0.21 | 0.53±0.04 | 4.03±0.44 | 588.60±6.55 |
| | 'Fetească neagră' | 2014 | 85.97±2.53 | 100.16±2.00 | 619.39±4.33 | 37.16±5.24 | 11.99±0.65 | 0.42±0.08 | 2.92±0.24 | 0.83±0.16 | 6.97±0.51 | 839.95±5.55 |
| | | 2015 | 65.90±2.19 | 99.86±1.20 | 621.15±4.80 | 36.89±0.30 | 12.09±0.19 | 0.85±0.07 | 3.34±0.27 | 0.81±0.13 | 5.50±0.46 | 757.48±3.43 |
| | | 2016 | 82.24±1.26 | 101.62±0.64 | 601.03±2.44 | 39.12±2.39 | 12.71±0.49 | 0.74±0.04 | 4.26±0.56 | 0.82±0.06 | 5.23±0.38 | 809.22±3.38 |
| | 'Fetească albă' | 2014 | 70.28±1.87 | 102.41±1.21 | 296.49±6.08 | 40.45±1.62 | 12.26±1.00 | 0.55±0.12 | 4.44±0.26 | 0.34±0.08 | 4.38±0.65 | 576.07±6.21 |
| | | 2015 | 49.85±3.36 | 100.69±2.01 | 267.36±9.63 | 38.00±1.38 | 12.27±1.00 | 0.72±0.05 | 3.20±0.34 | 0.67±0.11 | 4.82±0.78 | 622.48±8.37 |
| | | 2016 | 69.15±5.48 | 104.75±1.01 | 281.89±5.77 | 41.18±1.51 | 13.96±0.34 | 0.62±0.03 | 3.40±0.14 | 0.71±0.13 | 5.17±0.06 | 651.13±4.99 |
| | 'Fetească regală' | 2014 | 70.47±7.53 | 119.16±2.06 | 250.11±4.53 | 41.02±1.76 | 13.81±1.18 | 0.62±0.07 | 1.90±0.31 | 0.49±0.11 | 6.36±0.80 | 653.25±2.96 |
| | | 2015 | 85.52±0.91 | 123.73±1.21 | 273.45±9.11 | 39.28±2.58 | 12.08±0.67 | 0.53±0.03 | 2.55±0.21 | 0.22±0.03 | 5.25±0.31 | 648.71±2.70 |
| | | 2016 | 89.18±2.34 | 130.06±5.39 | 275.45±12.62 | 40.39±2.51 | 12.26±0.95 | 0.79±0.02 | 2.67±0.21 | 0.61±0.07 | 5.23±0.30 | 582.45±5.22 |
| | 'Băbească gri' | 2014 | 42.24±3.01 | 102.11±1.68 | 262.40±11.75 | 40.90±1.69 | 11.71±1.75 | 0.86±0.02 | 4.54±0.16 | 0.55±0.17 | 3.96±0.09 | 458.08±8.03 |
| | | 2015 | 49.76±3.57 | 99.86±1.30 | 276.44±10.69 | 38.75±1.15 | 12.21±0.97 | 0.79±0.02 | 4.39±0.67 | 0.45±0.20 | 3.04±0.06 | 461.42±1.86 |
| | | 2016 | 67.10±3.61 | 101.30±1.21 | 281.82±2.50 | 41.58±0.87 | 10.18±0.76 | 0.80±0.02 | 2.98±0.54 | 0.60±0.05 | 4.29±0.23 | 481.05±7.76 |
| | 'Şarba' | 2014 | 71.09±2.77 | 119.98±1.39 | 177.40±14.09 | 32.28±3.07 | 10.27±0.36 | 0.24±0.06 | 2.68±0.25 | 0.97±0.02 | 6.39±0.97 | 647.48±4.10 |
| | | 2015 | 40.97±6.07 | 116.75±2.75 | 209.15±3.08 | 31.35±1.25 | 11.65±1.05 | 0.48±0.03 | 3.37±0.18 | 0.82±0.05 | 7.02±0.40 | 568.34±3.53 |
| | | 2016 | 67.63±3.17 | 117.60±1.32 | 189.76±1.42 | 31.92±2.19 | 12.28±1.04 | 0.54±0.04 | 2.61±0.06 | 0.85±0.10 | 7.77±0.53 | 669.82±5.61 |
| | 'Aligoté' | 2014 | 39.62±2.79 | 97.12±6.64 | 189.27±4.69 | 38.56±0.63 | 12.29±0.98 | 0.22±0.04 | 3.28±0.15 | 0.37±0.17 | 6.63±2.63 | 425.92±5.18 |
| | | 2015 | 28.32±3.08 | 101.15±1.39 | 210.42±4.55 | 34.81±1.02 | 13.25±0.94 | 0.56±0.08 | 4.76±0.19 | 0.21±0.03 | 6.23±0.81 | 419.05±2.32 |
| | | 2016 | 43.47±1.23 | 99.78±1.26 | 239.81±2.99 | 50.50±0.84 | 12.89±1.48 | 0.63±0.04 | 3.67±1.32 | 0.38±0.16 | 5.93±0.63 | 459.18±9.67 |
| | 'Sauvignon blanc' | 2014 | 89.11±1.93 | 109.29±1.26 | 176.49±10.03 | 39.82±1.36 | 13.19±0.79 | 0.90±0.04 | 4.07±0.08 | 0.72±0.05 | 3.93±0.26 | 199.29±8.36 |
| | | 2015 | 76.78±2.97 | 113.90±1.4 | 167.03±6.83 | 41.03±1.37 | 13.24±0.92 | 0.81±0.06 | 2.96±0.68 | 0.66±0.02 | 4.57±0.38 | 219.28±3.19 |
| | | 2016 | 75.05±5.98 | 129.19±7.65 | 183.49±5.40 | 40.84±1.72 | 12.04±0.51 | 0.75±0.05 | 3.27±0.06 | 0.65±0.08 | 6.00±0.29 | 230.55±4.52 |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 'Muscat Ottonel' | 2014 | 62.08±6.89 | 113.27±4.31 | 213.06±7.09 | 42.58±3.79 | 11.33±0.11 | 0.52±0.08 | 2.36±0.21 | 0.23±0.03 | 7.34±1.04 | 266.12±5.93 |
| | 2015 | 53.84±3.92 | 100.37±1.99 | 199.95±1.48 | 45.51±3.67 | 13.25±0.89 | 0.71±0.06 | 1.34±0.19 | 0.44±0.12 | 6.52±0.18 | 287.05±7.82 |
| | 2016 | 63.28±4.88 | 101.08±1.36 | 192.20±.643 | 45.22±3.96 | 10.66±1.48 | 0.69±0.05 | 3.57±0.42 | 0.30±0.01 | 6.50±0.54 | 309.75±3.60 |
| 'Italian Riesling' | 2014 | 58.79±2.34 | 107.06±2.59 | 301.82±2.50 | 39.27±2.04 | 13.38±0.88 | 0.32±0.03 | 4.45±0.19 | 0.56±0.09 | 6.15±0.34 | 367.02±3.74 |
| | 2015 | 63.23±2.76 | 109.99±1.65 | 279.95±4.42 | 41.93±0.70 | 10.33±0.89 | 0.49±0.02 | 2.40±0.36 | 0.55±0.04 | 5.75±1.09 | 419.06±3.06 |
| | 2016 | 49.75±1.44 | 110.72±1.88 | 301.39±2.90 | 46.19±3.23 | 12.44±0.18 | 0.57±0.07 | 3.69±0.24 | 0.49±0.02 | 5.08±0.16 | 429.74±6.26 |
| Sig. | | $p \leq 0.000$ | $p \leq 0.000$ | $p \leq 0.000$ | $p \leq 0.000$ | $p \leq 0.000$ | $p \leq 0.000$ | $p \leq 0.000$ | $p \leq 0.000$ | $p \leq 0.000$ | $p \leq 0.000$ |
| Area | | *** | *** | *** | *** | ** | ** | *** | *** | *** | *** |
| Variety | | *** | *** | *** | *** | *** | *** | *** | *** | *** | *** |
| Years | | *** | *** | *** | *** | ns | *** | *** | ns | ns | *** |
| Area x Variety | | *** | *** | *** | *** | *** | *** | *** | *** | *** | *** |
| Area x Years | | *** | *** | ** | ns | ns | ** | *** | ns | * | *** |
| Variety x Years | | *** | *** | *** | *** | *** | *** | *** | *** | *** | *** |
| Sig. | | *** | *** | *** | *** | *** | *** | *** | *** | *** | *** |

M.P.L - maximum permissible limit (OIV, 2005). LOQ - lower than the limit of quantification. ns = insignificant.

## Appendix 2. Total metal concentration from wine samples

| Area | Variety | Year | Total metal concentration | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Ag (μg/L) | Al (μg/L) | As (μg/L) | Be (μg/L) | Bi (μg/L) | Cd (μg/L) | Ba (μg/L) | Cr (μg/L) | Cs (μg/L) | Ga (μg/L) |
| | | | M.A.L. | M.A.L. | M.A.L. | M.A.L. | M.A.L. | M.A.L. | M.A.L. | M.A.L. | M.A.L. | M.A.L. |
| | | | - | - | 0.2 mg/L | - | - | 0.01 mg/L | - | - | - | - |
| Dealu Bujorului | 'Merlot' | 2014 | 19.74±1.59 | 517.20±6.58 | 13.24±0.61 | 0.24±0.06 | 8.75±0.98 | 0.12±0.01 | 178.67±6.03 | 482.22±5.44 | 6.98±0.29 | 2.52±0.14 |
| | | 2015 | 15.63±1.03 | 441.81±5.47 | 14.46±1.18 | LOQ | 10.38±0.81 | 0.10±0.01 | 171.09±1.36 | 431.19±2.20 | 7.57±1.22 | 3.16±0.05 |
| | | 2016 | 15.82±0.37 | 626.11±9.77 | 12.07±0.72 | 0.19±0.04 | 5.74±0.79 | LOQ | 189.95±5.00 | 518.52±6.10 | 10.56±0.54 | 3.56±0.09 |
| | 'Fetească neagră' | 2014 | 13.44±2.55 | 686.02±7.91 | 10.05±0.34 | 0.28±0.04 | 10.50±0.95 | 0.14±0.02 | 178.02±5.35 | 352.60±3.90 | 7.01±1.24 | 4.21±0.12 |
| | | 2015 | 17.56±0.90 | 683.81±4.05 | 11.49±0.86 | 0.15±0.02 | 2.91±0.48 | 0.12±0.01 | 194.30±382 | 297.27±6.78 | 6.40±0.34 | 3.32±0.11 |
| | | 2016 | 16.60±1.61 | 487.85±7.93 | 11.29±1.00 | 0.17±0.02 | 2.98±0.22 | 0.11±0.01 | 187.26±1.51 | 409.39±2.44 | 9.95±0.30 | 4.22±0.03 |
| | 'Fetească albă' | 2014 | 11.56±0.57 | 469.55±6.15 | 6.09±0.51 | 0.03±0.02 | 10.16±1.90 | 0.09±0.02 | 191.68±2.28 | 872.42±2.93 | 14.48±0.81 | 4.29±0.07 |
| | | 2015 | 9.62±0.62 | 514.10±2.04 | 6.45±1.05 | LOQ | LOQ | 0.11±0.01 | 189.45±1.91 | 733.04±7.56 | 14.70±0.97 | 3.40±0.22 |
| | | 2016 | 12.07±0.46 | 518.97±2.34 | 7.97±0.33 | LOQ | LOQ | LOQ | 182.46±6.66 | 832.94±3.76 | 12.76±0.53 | 4.24±0.08 |
| | 'Fetească regală' | 2014 | 14.52±0.50 | 214.08±4.67 | 13.61±0.96 | LOQ | LOQ | LOQ | 173.86±1.30 | 762.37±5.93 | 11.54±0.51 | 1.46±0.08 |
| | | 2015 | 17.91±2.05 | 311.81±5.36 | 12.00±0.67 | LOQ | LOQ | 0.08±0.01 | 183.94±4.30 | 821.95±3.53 | 11.17±1.05 | 2.22±0.12 |
| | | 2016 | 17.09±0.42 | 291.93±6.44 | 9.63±0.21 | 0.13±0.02 | 1.37±0.17 | 0.12±0.01 | 180.72±0.94 | 818.18±2.96 | 10.49±0.67 | 1.79±0.09 |
| | 'Băbească gri' | 2014 | 31.93±3.43 | 420.39±3.72 | 5.71±0.60 | 0.42±0.14 | 2.15±0.16 | 0.09±0.02 | 187.33±1.59 | 699.09±4.74 | 8.93±0.17 | 2.68±0.06 |
| | | 2015 | 32.18±3.11 | 355.60±6.02 | 6.53±0.23 | 0.45±0.08 | 3.25±0.01 | 0.11±0.02 | 190.85±5.01 | 723.72±6.67 | 9.75±0.43 | 2.49±0.11 |
| | | 2016 | 28.63±1.02 | 521.31±2.33 | 7.90±0.65 | 0.26±0.04 | 3.27±0.05 | 0.17±0.02 | 168.19±4.01 | 1017.27±7.08 | 10.62±0.56 | 2.53±0.05 |
| | 'Şarba' | 2014 | 29.35±2.07 | 309.89±10.17 | 8.39±0.51 | 0.17±0.02 | 2.32±0.86 | 0.09±0.01 | 144.80±4.84 | 945.66±3.12 | 17.76±0.76 | 4.22±0.09 |
| | | 2015 | 27.26±0.54 | 349.24±6.91 | 7.74±0.65 | 0.29±0.06 | LOQ | LOQ | 136.42±2.06 | 967.51±3.51 | 16.44±0.20 | 5.36±0.17 |
| | | 2016 | 26.71±2.58 | 290.55±3.64 | 4.93±0.31 | 0.16±0.02 | LOQ | 0.11±0.01 | 156.72±6.05 | 329.16±5.32 | 14.13±0.46 | 4.85±0.06 |
| | 'Aligoté' | 2014 | 17.41±0.76 | 164.12±5.96 | 6.06±0.39 | 0.53±0.15 | 4.49±1.20 | LOQ | 170.04±3.92 | 419.21±6.65 | 6.63±0.45 | 5.11±0.02 |
| | | 2015 | 16.56±0.96 | 183.62±3.59 | 5.56±0.38 | 0.53±0.07 | LOQ | 0.13±0.01 | 167.38±4.36 | 517.73±9.30 | 9.20±0.31 | 4.53±0.17 |
| | | 2016 | 16.48±0.76 | 198.82±2.55 | 6.86±0.63 | 0.28±0.03 | 1.27±0.04 | 0.19±0.02 | 163.42±3.50 | 620.04±5.44 | 10.51±0.68 | 4.30±0.05 |
| | 'Sauvignon blanc' | 2014 | 27.49±1.39 | 273.25±7.96 | 20.20±1.94 | 0.20±0.05 | 11.16±1.35 | LOQ | 189.48±4.85 | 318.77±5.86 | 11.72±0.81 | 3.01±0.03 |
| | | 2015 | 26.45±0.98 | 403.95±6.47 | 19.67±1.66 | 0.24±0.02 | 10.18±1.16 | 0.08±0.01 | 177.76±5.45 | 415.54±3.15 | 9.62±0.63 | 2.69±0.41 |
| | | 2016 | 25.25±1.04 | 330.68±6.27 | 17.44±1.56 | 0.15±0.03 | 10.38±0.80 | 0.07±0.01 | 178.09±1.50 | 513.48±3.54 | 11.66±1.21 | 4.02±0.04 |
| | 'Muscat Ottonel' | 2014 | 19.07±0.60 | 268.17±3.52 | 8.21±0.54 | LOQ | 1.79±1.36 | 0.11±0.02 | 179.44±4.78 | 842.39±2.93 | 10.61±0.39 | 3.46±0.20 |
| | | 2015 | 21.36±1.12 | 238.25±5.81 | 8.23±1.28 | 0.14±0.02 | 2.23±0.09 | LOQ | 173.24±2.94 | 916.93±5.67 | 11.64±0.71 | 3.47±0.09 |
| | | 2016 | 17.08±1.29 | 246.08±7.95 | 10.75±1.43 | LOQ | LOQ | LOQ | 184.86±4.95 | 869.35±6.77 | 10.04±0.14 | 3.55±0.11 |
| | 'Italian Riesling' | 2014 | 21.18±1.42 | 530.79±2.13 | 13.30±0.61 | LOQ | 3.87±1.13 | 0.13±0.01 | 196.28±5.74 | 1129.64±6.00 | 13.31±0.30 | 4.25±0.08 |
| | | 2015 | 20.42±2.00 | 615.38±8.48 | 13.36±0.80 | LOQ | 2.34±0.21 | 0.10±0.02 | 185.16±5.83 | 1054.40±19.20 | 11.91±0.58 | 4.26±0.05 |
| | | 2016 | 21.12±1.50 | 621.11±1.30 | 12.06±0.53 | 0.11±0.01 | LOQ | 0.18±0.01 | 190.31±1.80 | 1221.75±10.83 | 11.03±0.56 | 4.23±0.01 |
| Murfatlar | 'Merlot' | 2014 | 22.68±1.45 | 479.38±4.61 | 10.70±1.36 | 0.29±0.04 | 3.21±0.05 | 0.29±0.02 | 169.81±1.34 | 458.85±5.46 | 14.63±1.00 | 4.40±0.14 |
| | | 2015 | 12.11±2.20 | 532.98±3.51 | 10.37±0.82 | 0.36±0.05 | 4.41±0.42 | 0.27±0.02 | 155.72±5.09 | 533.28±5.64 | 12.52±1.05 | 4.17±0.05 |
| | | 2016 | 29.21±1.88 | 540.27±3.53 | 9.90±0.30 | 0.26±0.03 | 5.18±0.17 | 0.26±0.06 | 169.69±1.53 | 598.75±2.44 | 11.27±1.04 | 5.58±0.62 |
| | 'Fetească neagră' | 2014 | 15.96±1.18 | 213.81±3.27 | 8.50±0.94 | 0.45±0.24 | 2.69±0.41 | 0.29±0.02 | 191.82±2.50 | 439.92±7.82 | 12.06±0.71 | 2.78±0.30 |
| | | 2015 | 13.33±0.81 | 360.90±4.67 | 10.04±0.33 | 0.30±0.02 | 2.59±0.90 | 0.26±0.04 | 181.78±2.15 | 566.03±4.88 | 13.03±0.36 | 3.21±0.04 |
| | | 2016 | 15.14±1.02 | 281.96±6.09 | 10.34±0.81 | 0.25±0.03 | 2.90±0.35 | 0.29±0.03 | 178.13±5.24 | 524.09±10.24 | 11.67±0.77 | 2.48±0.15 |
| | 'Fetească albă' | 2014 | 14.85±1.65 | 433.42±4.90 | 12.79±0.74 | 0.27±0.05 | LOQ | 0.39±0.02 | 178.76±3.05 | 672.85±3.66 | 11.82±0.89 | 2.47±0.14 |
| | | 2015 | 13.02±0.40 | 513.08±3.27 | 13.29±0.63 | LOQ | LOQ | 0.38±0.01 | 148.84±2.87 | 726.85±6.29 | 6.92±0.24 | 3.34±0.19 |
| | | 2016 | 10.33±0.74 | 493.61±5.30 | 10.47±0.22 | LOQ | 2.41±0.13 | 0.23±0.04 | 155.44±2.42 | 731.65±4.64 | 10.22±1.00 | 2.43±0.12 |
| | 'Fetească regală' | 2014 | 16.61±0.95 | 182.92±7.66 | 11.42±0.87 | 0.17±0.03 | 4.77±0.55 | 0.18±0.01 | 150.18±4.81 | 722.53±3.56 | 11.61±0.65 | 2.79±0.40 |
| | | 2015 | LOQ | 149.25±4.48 | 9.86±0.34 | LOQ | 5.43±0.40 | 0.16±0.02 | 164.47±5.03 | 654.30±5.03 | 10.31±1.56 | 1.80±0.44 |
| | | 2016 | LOQ | 312.20±4.82 | 13.47±0.75 | LOQ | LOQ | LOQ | 170.15±3.77 | 689.65±10.00 | 9.53±0.50 | 2.05±0.10 |
| | 'Băbească gri' | 2014 | 20.87±1.69 | 328.95±3.02 | 9.47±0.84 | 0.50±0.05 | 3.28±0.05 | 0.11±0.02 | 171.54±6.31 | 666.95±6.31 | 12.01±0.35 | 3.22±0.05 |
| | | 2015 | 15.04±3.31 | 263.99±6.67 | 10.72±0.73 | 0.33±0.04 | 2.40±0.23 | LOQ | 163.34±5.10 | 520.96±2.31 | 5.36±1.12 | 3.22±0.04 |
| | | 2016 | 15.59±2.67 | 420.39±1.03 | 10.37±0.30 | 0.59±0.05 | LOQ | 0.25±0.03 | 156.02±3.13 | 726.12±3.64 | 9.26±0.34 | 2.99±0.04 |
| | 'Şarba' | 2014 | 14.41±1.98 | 355.76±5.85 | 14.96±1.53 | 0.14±0.02 | 1.71±0.74 | 0.14±0.01 | 177.71±2.00 | 820.01±1.30 | 14.21±1.03 | 4.11±0.08 |
| | | 2015 | 9.76±1.19 | 419.19±6.61 | 12.73±0.47 | LOQ | LOQ | LOQ | 184.56±2.43 | 816.57±4.37 | 12.11±0.58 | 4.09±0.50 |
| | | 2016 | 11.26±1.04 | 369.58±7.18 | 11.76±1.73 | 0.23±0.02 | LOQ | 0.07±0.02 | 189.95±5.55 | 781.83±2.53 | 11.37±1.17 | 4.38±0.15 |
| | 'Aligoté' | 2014 | 22.49±1.11 | 218.29±4.13 | 4.64±0.05 | 0.49±0.03 | 3.90±0.66 | LOQ | 150.18±4.81 | 424.45±7.18 | 11.46±0.37 | 5.56±0.72 |
| | | 2015 | 32.26±1.95 | 181.59±3.00 | 7.12±0.67 | 0.54±0.03 | 3.49±0.20 | 0.12±0.02 | 162.01±2.84 | 526.97±6.66 | 13.12±0.57 | 5.88±0.56 |
| | | 2016 | 28.08±0.90 | 262.09±4.74 | 7.66±0.92 | 0.37±0.16 | 2.43±0.12 | 0.10±0.02 | 159.69±1.56 | 569.95±8.42 | 9.38±0.34 | 4.87±0.43 |
| | 'Sauvignon blanc' | 2014 | 28.12±2.86 | 432.52±4.01 | 14.26±0.53 | 0.31±0.04 | 7.67±0.19 | 0.12±0.01 | 160.31±5.95 | 510.56±1.55 | 12.95±0.34 | 3.03±0.16 |
| | | 2015 | 26.54±1.02 | 431.98±2.08 | 11.27±1.53 | 0.15±0.03 | 8.36±0.72 | 0.15±0.01 | 160.98±3.69 | 620.41±7.81 | 10.65±0.67 | 2.41±0.13 |
| | | 2016 | 19.45±0.76 | 511.46±1.56 | 10.14±0.36 | 0.13±0.02 | 9.13±0.37 | 0.16±0.02 | 166.27±4.55 | 620.85±1.06 | 7.10±0.77 | 4.89±0.28 |
| | 'Muscat | 2014 | 12.00±0.66 | 200.86±1.95 | 11.99±0.64 | LOQ | 2.86±0.69 | LOQ | 154.46±5.01 | 799.21±3.38 | 10.08±0.39 | 2.77±0.12 |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Ottonel' | 2015 | 9.96±0.29 | 240.49±5.58 | 10.42±0.81 | LOQ | LOQ | 0.09±0.01 | 161.34±3.73 | 811.97±2.09 | 7.32±0.76 | 3.31±0.23 |
| | | 2016 | 13.24±0.92 | 274.05±3.60 | 10.84±1.53 | 0.13±0.02 | LOQ | 0.07±0.02 | 163.20±5.46 | 791.27±2.81 | 5.80±1.29 | 3.12±0.13 |
| | 'Italian Riesling' | 2014 | 12.28±2.11 | 564.42±6.40 | 8.56±0.63 | 0.16±0.03 | 2.43±0.19 | 0.14±0.02 | 139.01±3.01 | 819.24±2.44 | 11.62±1.48 | 3.41±0.21 |
| | | 2015 | 11.56±1.51 | 611.09±1.36 | 9.84±0.33 | 0.25±0.01 | 2.65±0.57 | 0.14±0.01 | 138.98±2.57 | 822.26±3.07 | 9.92±0.53 | 5.55±0.39 |
| | | 2016 | 13.41±0.95 | 596.30±5.77 | 10.88±0.60 | LOQ | 1.54±0.51 | 0.14±0.01 | 140.08±1.04 | 831.97±2.08 | 10.14±0.16 | 3.83±0.73 |
| Ștefănești-Argeș | 'Merlot' | 2014 | 13.91±0.78 | 434.08±7.20 | 5.89±0.58 | 0.26±0.04 | 0.76±0.20 | 0.18±0.02 | 131.62±4.38 | 431.62±5.17 | 10.26±0.96 | 3.79±0.71 |
| | | 2015 | 10.83±0.92 | 520.95±1.13 | 9.44±0.91 | 0.14±0.02 | LOQ | 0.19±0.02 | 130.85±1.06 | 538.96±2.17 | 9.62±0.62 | 4.05±0.15 |
| | | 2016 | 14.32±0.77 | 509.34±0.34 | 9.08±0.59 | 0.14±0.01 | LOQ | 0.16±0.02 | 130.77±5.94 | 431.08±1.37 | 12.98±1.30 | 4.19±0.17 |
| | 'Fetească neagră' | 2014 | 9.63±0.69 | 362.51±0.20 | 9.73±0.45 | 0.30±0.02 | 1.35±0.18 | 0.19±0.05 | 138.69±2.35 | 328.62±2.83 | 7.23±1.37 | 4.62±0.05 |
| | | 2015 | 9.30±0.36 | 224.59±6.21 | 9.22±0.31 | 0.41±0.10 | 2.46±0.85 | 0.20±0.02 | 140.39±1.50 | 434.07±6.33 | 8.92±0.33 | 2.83±0.64 |
| | | 2016 | 10.64±0.70 | 331.25±1.49 | 9.77±0.29 | 0.40±0.10 | 2.33±0.02 | 0.16±0.02 | 136.47±7.00 | 416.31±3.04 | 7.56±0.59 | 4.20±0.02 |
| | 'Fetească albă' | 2014 | 21.15±1.50 | 519.70±5.08 | 10.56±0.66 | 0.15±0.03 | 5.55±1.05 | 0.08±0.03 | 161.08±3.85 | 724.88±4.69 | 11.32±1.00 | 6.28±0.55 |
| | | 2015 | 21.27±1.03 | 615.53±2.66 | 12.15±0.63 | 0.30±0.02 | 5.62±1.05 | 0.07±0.02 | 168.95±2.32 | 822.88±3.54 | 11.95±1.75 | 5.36±0.11 |
| | | 2016 | 20.59±1.69 | 614.73±1.15 | 12.17±0.51 | 0.29±0.02 | 5.95±0.53 | 0.08±0.01 | 171.82±2.21 | 812.18±2.47 | 8.60±0.91 | 5.06±0.42 |
| | 'Fetească regală' | 2014 | 24.47±1.02 | 430.27±6.93 | 11.59±1.51 | 0.16±0.02 | 7.97±0.46 | 0.20±0.02 | 115.61±4.82 | 671.93±10.89 | 10.62±0.61 | 5.10±0.51 |
| | | 2015 | 25.04±3.23 | 245.53±5.97 | 9.92±0.32 | LOQ | 5.89±1.15 | LOQ | 116.21±2.00 | 567.62±4.74 | 12.10±0.75 | 3.06±0.17 |
| | | 2016 | 10.50±0.98 | 363.70±3.38 | 12.06±0.70 | 0.13±0.03 | 3.46±0.17 | LOQ | 124.95±4.20 | 681.46±5.03 | 14.60±1.00 | 4.84±0.17 |
| | 'Băbească gri' | 2014 | 9.63±0.69 | 740.07±5.08 | 16.79±1.48 | 0.42±0.04 | LOQ | 0.19±0.03 | 131.71±3.76 | 680.70±1.52 | 6.99±0.57 | 3.60±0.50 |
| | | 2015 | LOQ | 814.98±5.04 | 15.39±0.71 | 0.50±0.01 | LOQ | 0.19±0.02 | 136.16±4.52 | 722.72±3.37 | 9.03±0.60 | 4.29±0.04 |
| | | 2016 | 7.18±3.55 | 761.21±1.42 | 14.72±0.84 | 0.30±0.02 | LOQ | 0.21±0.02 | 136.85±6.29 | 802.40±3.49 | 9.38±0.85 | 4.18±0.03 |
| | 'Șarba' | 2014 | LOQ | 570.09±7.02 | 15.43±0.85 | 0.31±0.02 | LOQ | 0.27±0.05 | 148.84±2.87 | 722.61±2.62 | 11.22±0.95 | 3.22±0.35 |
| | | 2015 | 5.20±1.08 | 499.20±2.36 | 12.29±0.32 | 0.27±0.03 | LOQ | 0.30±0.02 | 136.80±4.53 | 732.64±2.59 | 10.62±0.65 | 2.59±0.29 |
| | | 2016 | LOQ | 572.75±3.29 | 14.01±0.64 | 0.31±0.05 | 1.19±0.09 | 0.30±0.01 | 142.46±0.17 | 662.41±7.56 | 12.31±1.03 | 2.55±0.10 |
| | 'Aligoté' | 2014 | 5.39±0.60 | 354.36±8.05 | 12.09±0.46 | 0.29±0.04 | 3.62±0.96 | LOQ | 132.59±6.96 | 492.50±3.66 | 9.20±0.39 | 4.92±0.29 |
| | | 2015 | 7.34±0.90 | 411.21±1.42 | 10.28±0.65 | LOQ | LOQ | 0.07±0.02 | 128.26±3.40 | 471.22±1.50 | 10.48±0.75 | 4.92±0.06 |
| | | 2016 | LOQ | 462.60±3.60 | 12.84±0.58 | LOQ | LOQ | 0.11±0.01 | 144.88±4.90 | 528.62±6.15 | 8.11±0.11 | 4.76±0.17 |
| | 'Sauvignon blanc' | 2014 | 9.67±2.65 | 133.69±7.82 | 14.38±0.99 | LOQ | 6.60±0.92 | 0.14±0.02 | 159.08±2.49 | 623.31±4.96 | 12.26±1.00 | 2.27±0.23 |
| | | 2015 | 11.36±1.01 | 292.32±4.80 | 12.08±0.45 | LOQ | 5.60±0.06 | LOQ | 144.57±5.79 | 689.57±8.73 | 11.64±0.63 | 3.50±1.11 |
| | | 2016 | 10.48±0.79 | 311.12±1.46 | 12.25±0.38 | 0.15±0.04 | LOQ | LOQ | 168.85±6.13 | 671.93±5.47 | 10.50±0.72 | 3.19±0.04 |
| | 'Muscat Ottonel' | 2014 | 20.89±1.07 | 354.65±9.26 | 12.46±1.15 | 0.13±0.02 | 3.36±0.18 | LOQ | 130.09±3.30 | 811.07±1.37 | 9.71±0.68 | 1.75±0.78 |
| | | 2015 | 21.78±0.47 | 431.26±1.48 | 9.62±0.62 | LOQ | LOQ | 0.12±0.01 | 132.28±4.11 | 786.18±3.22 | 11.29±1.05 | 2.31±0.41 |
| | | 2016 | 12.31±1.03 | 393.28±7.81 | 10.48±0.66 | 0.26±0.05 | LOQ | 0.13±0.02 | 138.30±2.56 | 794.62±8.69 | 12.12±0.21 | 2.23±0.07 |
| | 'Italian Riesling' | 2014 | 13.61±4.97 | 837.99±7.20 | 13.38±1.08 | 0.13±0.02 | 5.30±0.61 | 0.12±0.03 | 122.98±3.85 | 864.61±3.00 | 12.07±0.73 | 4.10±0.66 |
| | | 2015 | 13.71±1.98 | 812.61±7.00 | 12.79±0.74 | 0.14±0.04 | LOQ | 0.13±0.01 | 127.39±5.15 | 796.75±2.71 | 9.82±0.16 | 4.60±0.50 |
| | | 2016 | 10.04±0.33 | 786.32±5.77 | 14.12±0.79 | LOQ | LOQ | 0.11±0.01 | 125.39±5.89 | 851.54±4.17 | 13.89±0.68 | 4.28±0.03 |
| | Sig. | | p ≤ 0.000 | p ≤ 0.000 | p ≤ 0.000 | p ≤ 0.000 | p ≤ 0.000 | p ≤ 0.000 | p ≤ 0.000 | p ≤ 0.000 | p ≤ 0.000 | p ≤ 0.000 |
| | Area | | *** | *** | *** | *** | *** | ** | *** | *** | *** | *** |
| | Variety | | *** | *** | *** | *** | *** | *** | *** | *** | *** | *** |
| | Years | | *** | *** | *** | *** | ** | *** | *** | ns | *** | *** |
| | Area x Variety | | *** | *** | *** | *** | *** | *** | *** | *** | *** | *** |
| | Area x Years | | *** | *** | *** | *** | ** | *** | *** | ** | *** | *** |
| | Variety x Years | | *** | *** | *** | *** | *** | *** | *** | *** | *** | *** |
| | Sig. | | *** | *** | *** | *** | *** | *** | *** | *** | *** | *** |

M.P.L - maximum permissible limit (OIV, 2005). LOQ - lower than the limit of quantification. LOQ for Ag: 0.1499 µg/L, LOQ for Be: 0.0030 µg/L, LOQ for Bi:

## Appendix 3. Total metal concentration from wine samples

| Area | Variety | Year | Total metal concentration | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | In (µg/L) | Sr (µg/L) | Ni (µg/L) | Rb (µg/L) | Se (µg/L) | Tl (µg/L) | U (µg/L) | Zn (µg/L) | Hg (µg/L) | Pb (µg/L) |
| | | | M.A.L. | M.A.L. | M.A.L. | M.A.L. | M.A.L. | M.A.L. | M.A.L. | M.A.L. | M.A.L. | M.A.L. |
| | | | - | - | - | - | - | - | - | 5 mg/L | - | 0.15 mg/L |
| Dealu Bujorului | 'Merlot' | 2014 | 10.13±1.91 | 202.07±8.15 | 517.84±17.32 | 1548.84±21.15 | 32.21±1.00 | 1.85±0.63 | 0.24±0.06 | 2343.52±2.19 | 0.21±0.02 | 55.44±1.01 |
| | | 2015 | 10.47±0.69 | 186.85±6.29 | 545.87±40.36 | 1455.89±40.36 | 15.29±1.53 | 2.14±0.17 | 0.12±0.01 | 2130.95±1.87 | BLD | 51.26±1.05 |
| | | 2016 | 11.52±1.41 | 202.89±3.03 | 635.01±5.43 | 1642.68±8.96 | 24.53±1.14 | 2.29±0.23 | 0.21±0.02 | 2130.52±7.36 | 0.13±0.01 | 47.79±2.07 |
| | 'Fetească neagră' | 2014 | 11.69±0.59 | 258.64±7.19 | 728.74±2.47 | 1442.73±15.74 | 28.32±1.46 | 1.33±0.19 | 0.17±0.01 | 2578.22±12.21 | 0.42±0.06 | 21.41±0.99 |
| | | 2015 | 9.26±0.61 | 262.65±3.77 | 586.06±9.09 | 1444.03±9.09 | 32.06±0.70 | 1.22±0.04 | 0.12±0.01 | 2560.26±14.39 | 0.22±0.04 | 21.19±1.17 |
| | | 2016 | 9.24±0.37 | 284.33±8.09 | 593.21±21.30 | 1435.65±6.71 | 33.53±2.22 | 1.09±0.09 | LOQ | 2451.06±29.74 | 0.29±0.06 | 35.50±1.24 |
| | 'Fetească albă' | 2014 | 11.96±0.64 | 184.36±5.03 | 640.04±12.86 | 1736.87±7.35 | 33.42±0.97 | 1.01±0.02 | 0.30±0.02 | 3243.83±20.95 | LOQ | 33.46±1.01 |
| | | 2015 | 3.04±0.36 | 175.15±5.82 | 542.98±4.04 | 1841.82±8.06 | 20.45±1.00 | 2.45±0.39 | LOQ | 3531.28±18.55 | LOQ | 38.09±1.50 |
| | | 2016 | LOQ | 157.02±3.72 | 360.19±4.14 | 1652.02±21.60 | 27.59±0.97 | 1.46±0.11 | LOQ | 3221.19±9.36 | LOQ | 24.39±4.65 |
| | 'Fetească regală' | 2014 | 3.39±1.11 | 191.02±1.36 | 508.11±8.21 | 1138.00±6.61 | 51.60±0.66 | 0.78±0.20 | 0.47±0.04 | 3132.75±5.99 | 0.16±0.06 | 52.63±3.13 |
| | | 2015 | 4.49±0.79 | 208.97±2.03 | 603.88±7.34 | 1334.46±12.82 | 48.84±2.90 | 1.15±0.09 | 0.41±0.01 | 3268.00±14.57 | 0.14±0.01 | 52.28±0.99 |
| | | 2016 | 2.95±0.52 | 194.51±8.62 | 136.84±13.84 | 1427.30±4.49 | 53.97±1.79 | 1.11±0.05 | 0.19±0.02 | 2353.73±6.91 | 0.20±0.01 | 23.63±1.71 |
| | 'Băbească gri' | 2014 | 5.35±0.05 | 275.35±4.99 | 640.68±12.10 | 1785.98±8.52 | 41.96±0.61 | 1.32±0.04 | 0.13±0.02 | 1867.19±28.55 | 0.38±0.03 | 125.35±6.10 |
| | | 2015 | LOQ | 290.12±3.91 | 637.78±6.62 | 1644.41±10.38 | 20.71±0.93 | 1.37±0.15 | LOQ | 2136.51±7.95 | 0.23±0.12 | 98.98±0.58 |
| | | 2016 | LOQ | 284.04±4.45 | 682.82±7.88 | 1563.27±0.89 | 22.86±1.66 | 1.38±0.16 | 0.11±0.02 | 2267.84±16.60 | BLD | 116.78±13.87 |
| | 'Șarba' | 2014 | 19.92±1.42 | 303.72±6.62 | 535.41±9.54 | 1996.07±7.43 | 10.16±1.24 | 3.26±0.02 | 0.34±0.07 | 2143.63±7.24 | 0.18±0.05 | 101.40±1.84 |
| | | 2015 | 17.95±2.07 | 281.92±2.48 | 451.73±4.21 | 1654.19±26.72 | 13.09±1.27 | 2.58±0.24 | 0.18±0.05 | 1995.78±7.25 | BLD | 87.92±3.35 |
| | | 2016 | 12.49±0.12 | 311.17±4.52 | 529.72±15.30 | 1840.17±6.80 | 16.24±1.49 | 2.22±0.12 | 0.15±0.02 | 1877.19±17.00 | 0.15±0.03 | 94.95±5.08 |
| | 'Aligoté' | 2014 | 5.95±0.53 | 157.29±6.80 | 335.66±16.20 | 1438.06±6.94 | 20.11±1.46 | 1.52±0.16 | 0.29±0.08 | 2361.20±35.93 | 0.14±0.02 | 18.31±1.54 |
| | | 2015 | 5.84±1.12 | 171.38±4.36 | 414.79±2.14 | 1529.03±23.09 | 9.62±0.62 | 2.22±0.09 | 0.24±0.02 | 2235.63±20.04 | 0.09±0.01 | 21.08±1.36 |
| | | 2016 | 4.64±0.05 | 183.09±3.37 | 530.08±17.17 | 1353.16±26.08 | 21.51±2.00 | 2.81±0.22 | LOQ | 2226.92±9.76 | 0.12±0.01 | 20.38±0.82 |
| | 'Sauvignon blanc' | 2014 | LOQ | 211.88±3.27 | 339.65±21.72 | 1735.72±8.79 | 62.87±3.02 | 1.92±0.06 | 0.28±0.03 | 1005.46±16.55 | BLD | 37.95±1.54 |
| | | 2015 | 2.16±0.19 | 191.36±2.45 | 508.12±7.35 | 1849.62±39.62 | 61.61±0.56 | 2.33±0.27 | 0.13±0.02 | 993.20±7.03 | 0.10±0.02 | 25.92±2.43 |
| | | 2016 | 1.89±0.50 | 188.46±0.85 | 475.42±33.69 | 1752.87±42.95 | 50.71±0.93 | 2.14±0.02 | 0.13±0.05 | 1239.19±5.61 | BLD | 40.58±1.42 |

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 'Muscat Ottonel' | 2014 | 2.79±0.41 | 134.14±8.61 | 514.86±13.20 | 1258.22±27.50 | 53.06±2.23 | 0.25±0.11 | 0.15±0.02 | 1429.55±5.11 | 0.58±0.04 | 43.68±2.13 |
| | | 2015 | LOQ | 114.08±6.44 | 486.76±11.84 | 1334.29±18.82 | 52.58±2.29 | 0.64±0.07 | LOQ | 1525.29±75.02 | 0.35±0.06 | 48.82±2.88 |
| | | 2016 | LOQ | 162.29±5.84 | 452.49±28.73 | 1765.22±19.65 | 39.27±1.86 | 1.15±0.10 | LOQ | 1453.63±15.91 | 0.19±0.08 | 26.86±0.63 |
| | 'Italian Riesling' | 2014 | 1.39±0.18 | 230.04±6.96 | 466.08±8.61 | 1637.72±9.11 | 7.27±2.60 | 1.88±0.17 | LOQ | 2876.99±16.86 | 0.37±0.07 | 33.59±1.00 |
| | | 2015 | LOQ | 234.92±9.80 | 467.48±18.34 | 1346.43±15.18 | 10.76±1.97 | 1.69±0.16 | LOQ | 2540.62±6.91 | 0.32±0.04 | 42.63±1.52 |
| | | 2016 | LOQ | 269.69±3.22 | 536.40±26.97 | 1465.35±16.30 | 11.98±0.65 | 1.57±0.32 | LOQ | 2137.69±6.76 | 0.14±0.02 | 49.85±1.32 |
| | 'Merlot' | 2014 | 3.02±0.40 | 236.56±9.17 | 233.07±20.67 | 1363.64±23.04 | 17.32±4.53 | 1.34±0.17 | 0.32±0.03 | 4246.74±27.35 | BLD | 74.85±4.55 |
| | | 2015 | 3.22±0.06 | 249.02±7.56 | 159.18±14.17 | 1345.86±38.00 | 17.24±0.60 | 0.92±0.06 | LOQ | 4151.54±12.92 | 0.12±0.01 | 62.18±3.11 |
| | | 2016 | LOQ | 238.69±8.64 | 132.98±3.51 | 1436.74±17.49 | 12.76±1.64 | 1.03±0.04 | LOQ | 3664.52±17.03 | LOQ | 84.26±2.56 |
| | 'Fetească neagră' | 2014 | LOQ | 202.41±3.48 | 174.61±13.20 | 1262.31±16.67 | 21.69±0.58 | 1.00±0.03 | LOQ | 1859.59±32.33 | 0.24±0.01 | 47.85±2.99 |
| | | 2015 | 1.68±0.76 | 191.79±3.67 | 232.39±15.35 | 1554.83±15.49 | 14.19±1.68 | 1.04±0.03 | LOQ | 1799.87±1.35 | LOQ | 21.60±4.01 |
| | | 2016 | LOQ | 230.51±1.38 | 242.41±5.86 | 1285.95±14.81 | 16.63±0.96 | 2.22±0.12 | LOQ | 1777.85±15.42 | 0.16±0.03 | 36.89±0.49 |
| Murfatlar | 'Fetească albă' | 2014 | 5.73±0.56 | 133.72±2.21 | 352.18±29.65 | 1662.52±13.05 | 31.08±2.34 | 2.30±0.23 | 0.13±0.04 | 1665.62±16.24 | 0.15±0.02 | 27.85±5.81 |
| | | 2015 | 5.73±0.55 | 146.71±4.11 | 401.62±13.07 | 1441.44±12.96 | 31.44±1.02 | 2.14±0.01 | 0.15±0.05 | 1767.07±13.69 | 0.11±0.02 | 31.03±2.46 |
| | | 2016 | 4.65±0.44 | 149.35±2.05 | 410.98±1.19 | 1542.83±18.01 | 25.72±3.78 | 1.39±0.15 | LOQ | 1662.53±10.31 | 0.22±0.03 | 27.69±0.59 |
| | 'Fetească regală' | 2014 | 5.52±0.90 | 181.59±2.82 | 509.96±18.45 | 1269.48±7.29 | 30.48±1.32 | 1.34±0.19 | 0.30±0.02 | 2359.37±6.30 | 0.27±0.05 | 42.42±1.20 |
| | | 2015 | 3.24±0.02 | 192.17±2.46 | 489.64±10.00 | 1337.09±19.54 | 34.49±2.83 | 1.08±0.08 | 0.30±0.02 | 1435.29±3.84 | 0.20±0.03 | 47.43±2.85 |
| | | 2016 | 4.00±0.65 | 181.08±1.36 | 501.12±1.37 | 1354.52±2.83 | 34.52±2.87 | 2.08±0.03 | 0.31±0.26 | 1672.61±13.08 | LOQ | 41.81±2.52 |
| | 'Băbească gri' | 2014 | 5.48±0.88 | 292.42±7.86 | 524.23±11.32 | 1728.62±2.82 | 23.53±2.12 | 0.92±0.11 | LOQ | 1860.27±20.65 | 0.19±0.03 | 10.65±1.55 |
| | | 2015 | 2.83±0.64 | 254.61±6.20 | 522.54±9.38 | 1471.05±27.92 | 21.78±1.93 | 1.36±0.17 | LOQ | 1964.60±1.11 | 0.30±0.02 | 23.54±2.13 |
| | | 2016 | LOQ | 259.44±8.53 | 515.21±7.43 | 1607.06±66.30 | 21.41±0.88 | 1.36±0.14 | LOQ | 2131.39±7.83 | 0.26±0.03 | 13.38±2.81 |
| | 'Şarba' | 2014 | 12.32±1.06 | 289.19±2.02 | 623.49±10.26 | 1649.51±7.49 | 16.62±2.21 | 2.52±0.15 | 0.11±0.02 | 2366.71±19.62 | 0.30±0.02 | 21.81±0.44 |
| | | 2015 | 11.57±1.10 | 300.31±2.08 | 432.80±6.25 | 1461.09±19.22 | 16.59±0.92 | 1.72±0.35 | 0.14±0.01 | 2455.41±17.45 | 0.30±0.01 | 18.62±1.05 |
| | | 2016 | 10.81±0.44 | 293.93±6.04 | 453.63±13.21 | 1532.53±6.70 | 15.59±1.25 | 3.85±0.53 | LOQ | 2135.94±3.86 | 0.14±0.01 | 28.90±3.20 |
| | 'Aligoté' | 2014 | 2.29±1.00 | 208.55±1.87 | 440.29±14.30 | 1336.43±25.24 | 16.27±1.42 | 2.41±0.13 | 0.20±0.01 | 1893.54±4.25 | 0.14±0.01 | 22.65±2.65 |
| | | 2015 | LOQ | 149.80±3.30 | 223.98±11.15 | 1260.21±21.76 | 17.83±1.15 | 2.45±0.12 | LOQ | 1672.07±18.21 | LOQ | 24.19±3.88 |
| | | 2016 | LOQ | 188.47±3.48 | 228.09±24.49 | 1313.28±39.75 | 16.48±0.92 | 1.44±0.17 | LOQ | 1976.12±17.22 | 0.14±0.02 | 18.62±1.02 |
| | 'Sauvignon blanc' | 2014 | 3.32±0.82 | 163.32±7.48 | 126.39±4.26 | 1425.38±5.17 | 69.27±2.38 | 0.67±0.11 | 0.13±0.02 | 1359.45±5.44 | 0.37±0.03 | 41.18±4.50 |
| | | 2015 | 1.90±0.58 | 135.18±3.88 | 213.10±3.01 | 1515.63±69.25 | 56.72±2.18 | 1.30±0.13 | 0.12±0.01 | 1953.27±4.20 | 0.28±0.04 | 19.82±1.36 |
| | | 2016 | 2.59±0.59 | 171.82±2.51 | 214.95±1.12 | 1577.01±16.06 | 71.24±1.02 | 1.09±0.03 | LOQ | 1443.52±19.37 | 0.30±0.02 | 24.49±0.90 |
| | 'Muscat Ottonel' | 2014 | 3.57±0.59 | 146.62±6.15 | 227.78±5.61 | 1237.25±6.50 | 48.57±1.05 | 1.68±0.15 | 0.10±0.02 | 1439.52±15.21 | LOQ | 40.46±2.69 |
| | | 2015 | 2.16±0.19 | 163.02±7.01 | 224.61±6.96 | 1325.20±5.08 | 51.47±6.51 | 2.12±0.03 | LOQ | 1426.84±4.21 | LOQ | 44.15±2.50 |
| | | 2016 | 1.81±0.43 | 125.28±3.81 | 304.49±7.22 | 1346.75±12.91 | 51.98±0.65 | 2.27±0.09 | LOQ | 1238.09±6.86 | LOQ | 38.10±2.89 |
| | 'Italian Riesling' | 2014 | 5.03±0.40 | 202.65±9.64 | 525.76±11.61 | 1570.16±6.54 | 13.63±0.94 | 2.41±0.11 | LOQ | 3137.01±15.12 | 0.31±0.05 | 20.15±2.11 |
| | | 2015 | 6.18±0.25 | 192.65±6.08 | 505.22±6.50 | 1550.17±10.81 | 22.52±1.14 | 2.29±0.12 | LOQ | 2988.79±9.65 | 0.23±0.05 | 9.61±0.64 |
| | | 2016 | 5.41±0.73 | 190.27±3.79 | 648.23±10.90 | 1485.55±5.46 | 18.27±0.59 | 1.74±0.22 | LOQ | 2765.62±18.29 | LOQ | 12.09±0.46 |
| Ştefăneşti-Argeş | 'Merlot' | 2014 | 5.18±0.18 | 264.17±6.53 | 232.06±9.13 | 1557.49±33.40 | 20.98±1.88 | 2.60±0.48 | 0.12±0.01 | 3215.79±3.40 | 0.21±0.03 | 27.11±4.04 |
| | | 2015 | 4.99±0.34 | 274.65±5.90 | 185.75±5.91 | 1493.56±4.86 | 21.81±0.43 | 1.53±0.15 | LOQ | 3135.38±16.29 | 0.14±0.03 | 25.86±1.49 |
| | | 2016 | 3.69±0.75 | 233.00±5.75 | 193.29±3.20 | 1360.04±18.04 | 32.41±1.05 | 2.50±0.42 | LOQ | 2896.95±2.56 | LOQ | 30.92±1.83 |
| | 'Fetească neagră' | 2014 | 4.70±0.40 | 186.47±7.30 | 236.43±14.90 | 1443.18±19.18 | 22.52±1.05 | 2.62±0.12 | 0.12±0.01 | 1879.19±17.15 | 0.14±0.02 | 29.81±1.34 |
| | | 2015 | 4.92±0.53 | 157.70±4.91 | 253.45±3.45 | 1242.49±12.59 | 22.58±1.48 | 1.98±0.09 | LOQ | 2123.49±13.50 | LOQ | 34.56±1.05 |
| | | 2016 | 2.83±0.45 | 177.82±9.44 | 231.95±3.52 | 1361.56±7.03 | 21.22±1.02 | 2.69±0.51 | LOQ | 1979.46±12.01 | LOQ | 15.60±1.08 |
| | 'Fetească albă' | 2014 | 4.96±0.37 | 134.91±5.06 | 525.32±6.66 | 1646.25±7.85 | 28.08±1.49 | 1.87±0.25 | LOQ | 1653.18±4.81 | 0.30±0.02 | 12.05±0.72 |
| | | 2015 | LOQ | 121.38±2.43 | 470.95±27.12 | 1521.82±79.24 | 26.64±0.89 | 1.98±0.09 | 0.09±0.02 | 1491.79±5.99 | 0.18±0.03 | 12.37±1.07 |
| | | 2016 | LOQ | 149.85±1.32 | 447.08±13.34 | 1638.33±44.20 | 24.52±1.14 | 2.09±0.21 | 0.09±0.04 | 1755.39±8.59 | 0.18±0.04 | 38.57±0.10 |
| | 'Fetească regală' | 2014 | 3.09±0.66 | 138.22±5.01 | 454.84±13.22 | 1126.32±8.33 | 18.44±2.43 | 2.08±0.09 | 0.13±0.02 | 2661.35±11.10 | LOQ | 49.82±1.36 |
| | | 2015 | 2.90±0.35 | 195.42±6.49 | 329.15±2.31 | 1250.40±42.89 | 20.29±1.78 | 2.66±0.37 | LOQ | 2599.86±1.35 | 0.19±0.04 | 49.95±1.48 |
| | | 2016 | 1.65±0.65 | 166.91±7.26 | 471.17±20.65 | 1341.74±19.46 | 20.05±1.35 | 2.08±0.63 | 0.12±0.01 | 2346.99±30.95 | LOQ | 61.19±1.39 |
| | 'Băbească gri' | 2014 | LOQ | 223.15±8.89 | 683.65±26.67 | 1451.63±21.04 | 16.48±0.92 | 0.93±0.37 | 0.22±0.03 | 1652.51±3.67 | 0.14±0.02 | 57.82±7.23 |
| | | 2015 | LOQ | 255.73±5.81 | 670.83±3.26 | 1248.60±14.97 | 15.37±2.23 | 1.38±0.16 | LOQ | 1646.30±10.49 | LOQ | 57.35±3.49 |
| | | 2016 | 1.08±0.13 | 279.12±4.46 | 681.02±3.00 | 1353.65±4.62 | 16.10±0.39 | 1.42±0.10 | LOQ | 1570.63±7.64 | LOQ | 52.06±2.89 |
| | 'Şarba' | 2014 | 12.45±0.85 | 278.98±2.11 | 337.20±11.13 | 1145.96±37.84 | 49.48±1.84 | 2.19±0.26 | LOQ | 1975.61±12.16 | 0.26±0.07 | 69.84±3.70 |
| | | 2015 | 12.05±0.70 | 239.39±7.38 | 326.86±.99 | 1236.86±15.80 | 49.48±1.85 | 2.15±0.02 | 0.15±0.01 | 1862.51±6.90 | 0.19±0.04 | 52.14±3.04 |
| | | 2016 | 10.29±0.29 | 218.98±5.03 | 353.29±4.21 | 1233.62±5.31 | 51.08±1.36 | 2.00±0.03 | LOQ | 2135.96±10.05 | 0.13±0.03 | 48.95±1.13 |
| | 'Aligoté' | 2014 | 3.60±0.32 | 237.14±7.56 | 523.82±7.88 | 1744.31±16.00 | 19.95±1.48 | 4.31±0.22 | 0.13±0.02 | 1870.71±3.34 | 0.24±0.01 | 38.66±6.41 |
| | | 2015 | 1.72±0.55 | 199.88±1.38 | 765.82±5.96 | 1658.65±4.50 | 21.55±2.08 | 3.93±0.32 | 0.10±0.01 | 1846.12±19.02 | LOQ | 41.73±0.57 |
| | | 2016 | LOQ | 213.53±2.79 | 670.63±14.71 | 1536.79±23.01 | 21.09±1.36 | 4.01±0.02 | LOQ | 1960.82±26.24 | LOQ | 43.09±1.27 |
| | 'Sauvignon blanc' | 2014 | 2.69±0.41 | 183.48±5.38 | 322.38±2.77 | 1450.93±33.63 | 50.01±1.15 | 1.54±0.38 | 0.24±0.08 | 1444.65±10.53 | LOQ | 36.89±2.56 |
| | | 2015 | 2.33±0.34 | 200.54±5.42 | 319.06±5.68 | 1679.83±4.45 | 42.36±0.98 | 1.15±0.14 | LOQ | 1034.65±29.50 | LOQ | 47.93±1.55 |
| | | 2016 | 1.34±0.19 | 191.86±4.24 | 363.68±6.00 | 1553.10±42.60 | 48.47±2.43 | 1.71±0.03 | LOQ | 1239.13±5.25 | 0.15±0.03 | 39.81±1.34 |
| | 'Muscat Ottonel' | 2014 | 3.22±1.07 | 138.19±6.32 | 324.85±4.65 | 1240.30±8.17 | 71.37±1.13 | 2.43±0.10 | 0.07±0.04 | 1326.32±0.65 | 0.18±0.01 | 38.46±2.74 |
| | | 2015 | 4.05±0.68 | 119.95±6.41 | 343.49±19.13 | 1139.78±11.79 | 68.94±7.38 | 1.49±0.12 | LOQ | 1239.19±9.45 | 0.18±0.04 | 37.04±2.21 |
| | | 2016 | 2.52±0.15 | 128.35±2.53 | 189.29±10.46 | 1356.09±7.86 | 64.08±1.54 | 4.06±0.23 | LOQ | 1344.78±17.79 | LOQ | 35.91±0.59 |
| | 'Italian Riesling' | 2014 | 3.80±0.68 | 245.41±5.19 | 457.85±22.72 | 1532.87±41.46 | 22.38±1.08 | 2.81±0.27 | 0.13±0.01 | 2973.97±21.67 | 0.14±0.06 | 47.15±5.25 |
| | | 2015 | 4.06±0.46 | 224.12±7.16 | 597.22±16.49 | 1772.55±34.94 | 37.03±0.42 | 2.41±0.22 | LOQ | 3125.92±0.64 | LOQ | 50.72±0.94 |
| | | 2016 | 2.34±0.20 | 219.81±0.30 | 522.51±1.06 | 1681.06±23.11 | 28.23±0.65 | 2.37±0.26 | LOQ | 2885.63±17.38 | LOQ | 27.57±2.72 |
| | Sig. | | p ≤ 0.000 | p ≤ 0.000 | p ≤ 0.000 | p ≤ 0.000 | p ≤ 0.000 | p ≤ 0.000 | p ≤ 0.000 | p ≤ 0.000 | p ≤ 0.000 | p ≤ 0.000 |
| | Area | | *** | *** | *** | *** | *** | *** | *** | *** | *** | *** |
| | Variety | | *** | *** | *** | *** | *** | *** | *** | *** | *** | *** |
| | Years | | *** | *** | *** | *** | *** | *** | *** | *** | *** | *** |
| | Area x Variety | | *** | *** | *** | *** | *** | *** | *** | *** | *** | *** |
| | Area x Years | | *** | *** | *** | *** | *** | *** | *** | *** | *** | *** |
| | Variety x Years | | *** | *** | *** | *** | *** | *** | *** | *** | *** | *** |
| | Sig. | | *** | *** | *** | *** | *** | *** | *** | *** | *** | *** |

*M.P.L - maximum permissible limit (OIV, 2005). LOQ - lower than the limit of quantification. LOQ for In: 0.0100 µg/L, LOQ for U: 0.00842 µg/L,LOQ for Hg: 0.1379µg/L. ns = insignificant.