Levels of selected metals in wines from different Herzegovinian viticultural localities

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Summary

Concentrations of seven metals indicated as hazardous to human health (Pb, Cu, Zn, Mn, Ni, V, and Cr) were determined in 24 Hezegovinian white and red wines originating from four viticultural localities (Čitluk, Ljubuški, Stolac, and Trebinje). The concentrations of Pb, Cu, Mn, Ni, V, and Cr were determined by the ET AAS, and Zn concentrations were determined by the FAAS technique. Among seven measured metals, Zn and Mn were found in all analysed wines, while Ni was found in only four, and Cr in only five wines. Some wines contained metals at levels above the regulated maximum acceptable limits (Cu in four, Cr in three, Ni in two, and Pb in one wine). White wines from the Stolac locality were characterized by higher concentrations of Cu, Pb, and Zn. However, it was not possible to establish a firm link between the concentrations of the analysed metals and localities where grapes for wine production were grown for other wines.

Keywords: metals in wine, Herzegovina, atomic absorption spectrometry, viticultural localities

Introduction

Many metals are among the hundreds of different substancescommonly found in wines. In only one sample of wine (Australian Shiraz) Hague et al. (2008) detected 30 metals with a total concentration of more than 5600 mg/L. Metals enter a wine as a final product in different ways, while their concentrations and structure in wine depend on at least four groups of factors. The first, and frequently mentioned group, involves soil on which a vineyard is established, and the capacity of wine to absorb various mineral substances (Orescanin et al., 2003; Mirlean et al., 2007; Lai et al., 2010; Fiket et al., 2011). The second group is linked to the ways and conditions of a grape production, among which applications of pesticides and environmental air pollutions are frequently stressed (Eschnauer, 1982; Angelova et al., 1999; Mirlean et al., 2007; La Pera et al., 2008; Wightwick et al., 2008; Fiket et al., 2011). The third group of factors are those related to the realization of the alcoholic fermentation, and possibly added different oenological substances during the production of wine (Garrido et al., 1997; Al Nasir et al., 2001; Catarino et al., 2008; Volpe et al., 2009). The fourth group includes subsequent contaminations of wine with metals by the equipment used during the processing of grapes into wine, the characteristics of vessels for wine storage, including even the characteristics of a glass used for wine bottles (Eschnauer, 1982; Kaufmann, 1998; Cabrera-Vique et al., 1997; Teissèdre et al., 1998a; Teissèdre et al., 1998b; Almeida and Vasconcelos, 2003a; Kristl et al., 2003).

A number of researches suggested relations between the concentrations of metals in wines with wider or narrower geographic or geological origins of grapes (Kment et al., 2005; Galgano et al., 2008; Ražić and Onjia, 2010; Fiket et al., 2011; García-Rodríguez et al., 2011; Sen and Tokatli, 2014). It seems that these relations could easily be established for the concentrations of geogenic elements. However, due to a number of possible contaminations during the production of grapes and wines, and the storage of wines, linkages between metals in wine and wine origins are not always possible (Almeida and Vasconcelos, 2003b).

Metals in wine may have a number of roles: from positive or negative influences on organoleptic characteristics, through causes of their different instabilities, to the fact that wines can be considered sources of metals needed in the human diet. Besides the metals which are typically abundant in grapes (K, Ca, Mg), metals such as Fe, Cu, Zn, Mn, and Cr are necessary or useful in a series of physiological processes in wine yeasts and humans (Marais and Blackhurst, 2009). However, high concentrations of metals in wines, as well as in other foodstuffs, can jeopardize the consumer's health. The fact is that so

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far there have not been precise characterization of the impact of a number of metals found in foodstuffs on human health. Only Hg, Pb, and Cd are undoubtedly considered toxic, with a certain possibility of toxicity for Cu, Ni, Cr, V, Zn, Ag, and Al in high concentrations (Marais and Blackhurst, 2009). Consequently, the Organisation International de la Vigne et du Vin (OIV) established maximum acceptable limits for only a few elements in wine (Pb, Cd, Cu, Na, Zn, Ag, As, F, Br, F, and B; OIV International Code of Oenological Practices, 2015). In addition to those, some countries used to have regulations for the maximum acceptable limits of some other elements in wines, such as Sn, Fe, Ni, St, Al, Cr, and Mn (Croatian Government, 1996).

Although there had been allegations of health hazards due to metals in wine (Pedersen et al., 1994), a few years ago two articles by researchers from the Kingston University London (Hague et al., 2008; Naughton and Petróczi, 2008) indicating dangerously high concentrations of seven metals (Pb, Cu, Mn, Zn, Cr, Ni, and V) in wines from certain countries attracted considerable public attention. Dangers of high concentrations of these metals for the health of moderate wine consumers were expressed through the calculated high or very high values of the target hazard quotient (THQ). The results (particularly Naughton and Petróczi, 2008) had been challenged as methodologically incorrect (Curvelo-Garcia et al., 2009), and the authors themselves later corrected their results through significantly reduced values of the presented THQs (Naughton and Petróczi, 2009; Hague et al., 2010). Nevertheless, the articles seriously questioned the common "good health" reputation of wines.

In the recently available literature many results on concentrations of these seven metals in wines from different countries could be found. A number of researchers reported concentrations of Pb, Cu, and Zn (Lazos and Alexakis, 1989; Marin and Ostapczuk, 1992; Mena et al., 1997; Suturović and Marjanović, 1998; Galani-Nikolakaki et al., 2002; Kristl et al., 2003; Orescanin et al., 2003; Lara et al., 2005; Catarino et al., 2008; Galgano et al., 2008; La Pera et al., 2008; Bukovčan et al., 2009; Voica et al., 2009; Volpe et al., 2009; Kostić et al., 2010, Ražić and Onjia, 2010; García-Rodríguez et al., 2011; Tariba et al., 2011a; Tariba et al., 2011b; Woldemariam and Chandravanshi, 2011; Calin et al., 2012; Sen and Tokatli, 2014). Concentrations of Mn, Cr, and Ni are somewhat less frequently reported (Eschnauer, 1982; Lazos and Alexakis, 1989; Cabrera-Vique et al., 1997; Lendinez et al., 1998; Teissèdre et al., 1998a; Galani-Nikolakaki et al., 2002; Kristl et al., 2003; Orescanin et al., 2003; Lara et al., 2005; Catarino et al., 2008; Galgano et al., 2008; Bukovčan et al., 2009; Voica et al., 2009; Volpe et al., 2009; Ražić and Onjia, 2010; García-Rodríguez et al., 2011; Woldemariam and Chandravanshi, 2011; Sen and Tokatli, 2014), while reports on concentrations of vanadium in wines are sporadic (Teissèdre et al., 1998b; Galgano et al., 2008; García-Rodríguez et al., 2011). Pohl (2007) presented a useful compilation of research results on concentrations of metals in wines from a number of countries. With the partial exception of one study on the content of Zn (and Fe) in the regional white wines, involving a few Herzegovinian wines (Blesić et al., 2010), there were no available researches on these metals in wines originating from Bosnia and Herzegovina.

The aim of this study was to find concentrations of the challenged seven metals (Pb, Cu, Mn, Zn, Cr, Ni, and V) in white and red dry wines from the vintage 2010 originating from the four Herzegovinian viticultural localities, with an attempt toa classify wines by the content of the analysed metals and locality of origin.

Materials and methods

Materials

Wine samples of 12 white, and 12 red wines produced from grapes grown in 2010 were collected during March and April 2011. The samples came from four Herzegovina localities (municipalities), namely Čitluk, Ljubuški, Stolac and Trebinje (Fig. 1).

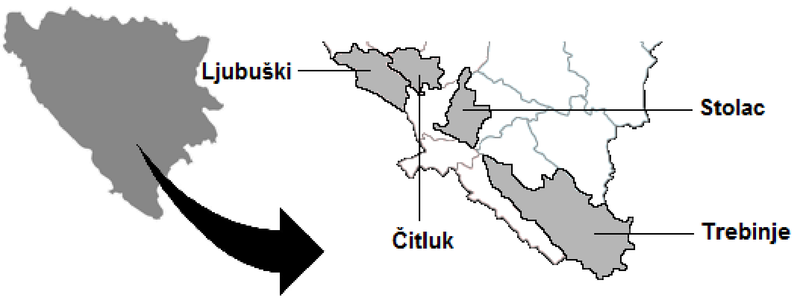

Fig. 1. Čitluk, Ljubuški, Stolac and Trebinje localities (municipalities) in Bosnia and Herzegovina

Three samples of white, and three samples of red wines were taken from each locality. Stolac and Čitluk wine samples came from one, Ljubuški from three, and Trebinje from two wineries. Ljubuški wine samples came from three, Trebinje from two, and Stolac and Čitluk from one winery each. On each locality, the wines originated either from grapes grown on different micro-localities, or from grapes of different varieties grown on the same micro-localities (Table 1).
The wines taken for the analysis were stored in stainless steel vessels. Each wine samples was taken from five vessels (one litre of wine from each vessel), so measurements of the analysed metals for each wine were done in five replications.

Analytical methods

Preparation of the wine samples and measurements of concentrations of lead, copper, manganese, chromium, vanadium, and nickel were performed according to the standards BAS EN 13804:2005 (EN 13804:2002); BAS EN 13805:2005 (EN 13805:2002) and BAS EN 14084:2005 (EN 14084:2003). Determination of zinc was performed according to the method OIV-MA-AS322-08 (direct measurement by the flame AAS after removal of alcohol from wine).

Microwave digestion was done on the Anton Paar 3000 MW (Anton Paar GmbH, Graz, Austria) digester, and rotary evaporation on the Buchi Rotavapor R-215 (Buchi Labortechnik AG, Flawil, Switzerland).
The concentrations of Pb, Cu, Mn, Cr, V, and Ni were measured by the ET AAS (electro thermal atomic absorption spectrometry) technique on the PerkinElmer - AAnalyst 800 (PerkinElmer Instruments, Norwalk, CT, USA), with auto sampler and Zeeman's graphite background correction (longitudinal background correction). Atomisation was done by argon, using a graphite tube with a platform, with an acetylene/air flame technique.
PerkinElmer pure standards of Pb, Cu, Mn, Cr, Ni, and Zn in a concentration of 1000 mg/L in 2% HNO_3 (Atomic Spectroscopy Standard, PerkinElmer Life and Analytical Sciences, Shelton, CT, USA) and V (vanadium) Trace Cert standard in concentration of 1000 mg/L in 3% HNO3 (Fluka, Sigma-Aldrich Chemie GmbH, Buchs, Switzerland) were used. As modifiers in the determination of Pb, Mn, Cr, Ni, Zn and Cu, $Mg(NO_3)_2$, (1% Mg as nitrate), and 10% $NH_4H_2PO_4$ (both modifiers: PerkinElmer Life and Analytical Sciences, Shelton, USA) were used.

Table 1. Localities, micro-localities and grape varieties used for the production of the analysed wines

Wine colour	Locality	Micro-locality	Variety	Mark used in this study
White wines	Čitluk	Vionica	Žilavka	W-C1
		Trtla	Chardonnay	W-C2
		Blizanci	Žilavka	W-C3
	Ljubuški	Radišići	Žilavka	W-L1
		Ljubuški	Žilavka	W-L2
		Crnopod	Žilavka	W-L3
	Stolac	Pjana brda	Žilavka	W-S1
		Prihvaćenice	Žilavka	W-S2
		Pješivac polje	Žilavka	W-S3
	Trebinje	Trebinjsko polje	Žilavka	W-T1
		Lastva	Žilavka	W-T2
		Bihovo	Chardonnay	W-T3
Red wines	Čitluk	Vionica	Blatina	R-C1
		Dubrava	C. Sauvignon	R-C2
		Dubrava	Blatina	R-C3
	Ljubuški	Radišići	Blatina	R-L1
		Otok	Blatina	R-L2
		Crnopod	Blatina	R-L3
	Stolac	Vidovo polje	Merlot	R-S1
		Vidovo polje	Vranac	R-S2
		Prihvaćenice	Vranac	R-S3
	Trebinje	Trebinjsko polje	Vranac	R-T1
		Zgonjevo	Vranac	R-T2
		Trebinjsko polje	Merlot	R-T3

In accordance with analytical protocols, 65% HNO_3 p.a., H_2O_2 min. 30% p.a. (both: Sigma-Aldrich Chemie GmbH, Steinheim, Germany), and Milli-Q water (18.2 MΩ · cm at 25°C) were used as auxiliaries.
The laboratory's detection limits of the analysed metals are presented in Table 2.

Statistical methods

Basic statistical analyses (descriptive statistics, ANOVA, LSD post-hoc test) were performed with the Bill Miller's Openstat software (version Dec 2014). PCA analysis was done with the statistical package StatBox 6.7 (Grimmer Soft, France).

Table 2. Detection limits of the analysed metals

Metal	Limit of detection (µg/l)	Analytical technique
Vanadium	0,1	ET AAS
Copper	0,014	ET AAS
Chromium	0,004	ET AAS
Manganese	0,005	ET AAS
Lead	0,05	ET AAS
Nickel	0,07	ET AAS
Zinc	1,5	F AAS

Table 3. Mean concentrations (µg/L) of Pb, Cu, Mn, Zn, Ni, V, and Cr in white (W) and red (R) Herzegovinian wines from Čitluk (C), Ljubuški (L), Stolac (S) and Trebinje (T) localities

Wine	Metal						
	Pb	Cu	Mn	Zn	Ni	V	Cr
W-C1	30 ± 1..3 d*	568 ± 3.5 d	869 ± 3.8 h	565 ± 7.7 i	nd**	nd	nd
W-C2	3 ± 0..3 g	95 ± 1.4 f	1541 ± 19.4 a	636 ± 0.8 e	nd	nd	nd
W-C3	1 ± 0..2 g	87 ± 0.5 f	1290 ± 6.7b	574 ± 1.1 h	nd	26 ± 1.0 a	nd
W-L1	12 ± 0.9 e	9 ± 0.7 g	892 ± 10.2 g	560 ± 1.6 i	nd	15 ± 1.5 c	nd
W-L2	7 ± 0.4 fg	28 ± 0.6 g	1003 ± 18.8 de	586 ± 1.7 g	nd	13 ± 0.6 c	nd
W-L3	6 ± 0.4 fg	nd	964 ± 9.4 f	370 ± 0.9 k	84 ± 1.4	nd	93 ± 5.1 a
W-S1	90 ± 1.4 c	**1359 ± 18.1 c**	1270 ± 13.8 b	2100 ± 5.6 a	nd	26 ± 1.2 a	48 ± 12.1 b
W-S2	95 ± 1.4 b	**1398 ± 5.6 b**	1041 ± 7.2 d	1427 ± 3.5 c	nd	22 ± 1.0 b	nd
W-S3	****189 ± 3.5 a**	**2874 ± 18 a**	1126 ± 3.2 c	2031 ± 1.3 b	nd	21 ± 0.6 b	nd
W-T1	8 ± 0.5 f	nd	1141 ± 9.8 c	618 ± 0.7 f	nd	nd	nd
W-T2	5 ± 0.6 fg	154 ± 1.4 e	822 ± 9.3 i	674 ± 1.5 d	nd	nd	nd
W-T3	8 ± 0.7 f	5 ± 0.4 g	1008 ± 8.1 de	396 ± 0.4 j	nd	nd	nd
R-C1	15 ± 1.6 de	344 ± 2.0 d	778 ± 6.1 j	576 ± 11.4 e	nd	nd	nd
R-C2	nd	82 ± 1.3 g	1711 ± 12.2 b	518 ± 2.1 f	nd	nd	nd
R-C3	18 ± 0.5 d	115 ± 0.7 f	950 ± 6.8 g	1022 ± 1.9 b	nd	37 ± 0.7 a	nd
R-L1	nd	4 ± 1.3 i	1120 ± 6.2 ef	470 ± 1.7 g	**489 ± 1.7** a	nd	**463 ± 2.3** b
R-L2	13 ± 0.5 e	3 ± 0.3 i	828 ± 5.2 i	778 ± 1.1 d	nd	16 ± 1.0 b	nd
R-L3	nd	nd	1154 ± 7.0 e	586 ± 0.8 e	nd	2 ± 0.6 d	nd
R-S1	30 ± 0.7 c	169 ± 8.4 e	1112 ± 6.0 f	526 ± 1.5 f	nd	nd	**752 ± 13.1** a
R-S2	48 ± 0.7 b	389 ± 2.3 c	894 ± 11.0 h	875 ± 2.5 c	nd	5 ± 1.3 c	nd
R-S3	58 ± 2.3 a	**1056 ± 11.7 a**	1922 ± 23.9 a	1861 ± 6.6 a	nd	nd	nd
R-T1	15 ± 0.6 de	55 ± 0.9 h	1366 ± 9.4 c	357 ± 0.9 h	**421 ± 13.4** b	2 ± 0.4 d	**732 ± 12.7** a
R-T2	4 ± 0.7 f	nd	1204 ± 23.1 d	478 ± 1.8 g	nd	nd	nd
R-T3	47 ± 0.5 b	856 ± 14.1 b	523 ± 9.4 k	1856 ± 4.8 a	44 ± 2.7 c	nd	nd

*LSD test ($p \leq 0.05$); different letters annotated to the means in the wine colour sub-column indicate statistically significant differences
**nd – Not detected.
***Underlined and bolded: means above maximum acceptable limits set by the OIV (Pb, Cu, Zn) or Croatian regulations (Ni, Cr).

Results and discussion

Concentrations of metals in wines

The average concentrations of the seven metals in the analysed wines are presented in Table 3. All analysed white wines, and nine of the twelve analysed red wines contained lead. The average content of Pb was higher in white (38 μg/L) than in red wines (28 μg/L). In only one wine (W-S3), the measured concentration of Pb was above the maximum acceptable limit set by the OIV (150 μg/L). Wines from the Stolac area contained considerably higher concentrations of Pb (the average of 85 μg/L) compared to wines from the three other localities, with worrying concentrations of lead in white wines (the average of 125 μg/L). The average concentration of Pb in wines from other localities was only 13 μg/L, which is below the average contents of Pb that are reported for some Croatian (46 μg/L, Bukovčan et al., 2009; 14 - 559 μg/L, Tariba et al., 2011a), Spanish (up to 1125 μg/L, Mena et al., 1997; 43 - 47 μg/L, García-Rodríguez et al., 2011), Argentinian (50 - 90 μg/L, Lara et al., 2005), Ethiopian (140 to 310 μg/L, Woldemariam and Chandravanshi, 2011), Serbian (130 - 270 μg/L, Suturović and Marjanović, 1998), Italian (33 - 46 μg/L, Galgano et al., 2008; 50 - 125 μg/L, Volpe et al., 2009), Cretan (180 - 420 μg/L, Galani-Nikolakaki et al., 2002), and Greek wines (230 μg/L, Lazos and Alexakis, 1989). However, the average concentration of Pb in white wines from the Stolac locality, with the exceptions of some Serbian (Suturović and Marjanović, 1998), Ethiopian (Woldemariam and Chandravanshi, 2011), Spanish (Mena et al., 1997), and Cretan wines (Galani-Nikolakaki et al., 2002), was higher than its concentration in wines reported in the available literature.

Copper was found in 20 out of 24 analysed wines, with an average concentration of 482 μg/L. On average, white wines contained more than double the concentrations of Cu (658 μg/L) than red wines (307 μg/L). The concentrations of Cu registered in all three whites, and one red wine (R-S3) from the Stolac locality were above the OIV's set maximum acceptable limit (1000 μg/L). Excluding wines from the Stolac locality, the average concentration of Cu in the remaining 14 wines was 172 μg/L, which is below or at the level of concentrations of this metal which were noted for some Croatian (180 μg/L, Bukovčan et al., 2009; Tariba et al., 2011b), Romanian (122 - 538 μg/L, Calin et al., 2012), Serbian (100 - 460 μg/L, Suturović and Marjanović, 1998; 70 - 570 μg/L, Kostić et al., 2010), Italian (96 - 249 μg/L, Galgano et al., 2008; 44 to 1112 μg/L, La Pera et al., 2008; 100 - 300 μg/L, Volpe et al., 2009), Cretan (200 - 600 μg/L, Galani-Nikolakaki et al., 2002), Greek (250 μg/L, Lazos and Alexakis, 1989), Ethiopian (500 - 1500 μg/L, Woldemariam and Chandravanshi, 2011), and Slovenian wines (110 μg/L for white and 370 μg/L for red wines, Kristl et al., 2003). Nevertheless, the average concentration of Cu in these 14 wines was higher than those reported for some Spanish (58 and 113 μg/L, García-Rodríguez et al., 2011), Argentinian (23 - 28 μg/L, Lara et al., 2005), and Central Balkan wines (up to 130 μg/L, Ražić and Onjia, 2010).

Manganese was found in all analysed wines, with an average concentration of 1105 μg/L. The average concentrations of Mn in wines from different locations were in a relatively narrow range (from 993 μg/L for Ljubuški to 1227 μg/L for Stolac), as well as its average concentrations in white (1081 μg/L) and red wines (1130 μg/L). The OIV have not regulated the maximum acceptable limit of Mn in wines, but it should be noted that the Chinese government has recently set it at 2000 μg/L. Although some global wine exporters consider this request unjustified, the analysed Herzegovinian wines meet it. The concentrations of Mn in the analysed Herzegovinian wines were comparable to those referred for some Italian (1040 - 1630 μg/L, Galgano et al., 2008), Ethiopian (104 - 1880 μg/L, Woldemariam and Chandravanshi, 2011), Slovenian (red wines: 1100 μg/L, Kristl et al., 2003), Spanish (979 and 1465 μg/L in two regions, García-Rodríguez et al., 2011), and Croatian wines (1250 μg/L, Bukovčan et al., 2009), but were above concentrations mentioned for some Central Balkan (280 - 550 μg/L, Ražić and Onjia, 2010), Turkish (only 0.44 to 2.2 μg/L, Sen and Tokatli, 2014) and Slovenian white wines (500 μg/L, Kristl et al., 2003).

Zinc was also found in all analysed wines in concentrations well below the maximum acceptable limit set by the OIV (5000 μg/L). The average concentrations of Zn calculated for all white (878 μg/L), and for all red wines (825 μg/L) were relatively uniform. Significantly higher concentrations of Zn were found in all three white and one red (R-S3) wine from Stolac, and in one red wine from Trebinje (R-T3). Consequently, wines from Stolac had on average remarkably higher concentrations of Zn (1470 μg/L) compared to its average concentrations in wines from other localities (from 558 μg/L for Ljubuski to 878 μg/L for Trebinje). Previously reported concentrations in only four analysed Herzegovinian wines were much lower, varying from 110 to 480 µg/L (Blesić et al., 2010). The concentrations of Zn in Herzegovinian wines analysed this time, especially in those from the Stolac locality, were above its concentrations reported in Argentinian (24 - 130 µg/L, Lara et al., 2005), Central Balkan (100 - 300 µg/L, Ražić and Onjia, 2010), Turkish (81 - 808 µg/L, Sen and Tokatli, 2014), Slovenian (Pinot noir: 400 µg/L, white wines: 600 µg/L, Kristl et al., 2003), Chilean (700 µg/L, Laurie et al., 2010), Serbian (160 - 790 µg/L, Suturović and Marjanović, 1998; 210 - 670 µg/L, Kostić et al., 2010), Croatian (716 µg/L, Bukovčan et al., 2009), Spanish (309 and 547 µg/L for wines from two regions, García-Rodríguez et al., 2011), Greek (410 µg/L, Lazos and Alexakis, 1989), and Italian wines (560 - 720 µg/L, Galgano et al., 2008; 300 - 600 µg/L in white wines, Volpe et al., 2009). The Zn concentrations higher than those found in the analysed Herzegovinian wines were reported for Ethiopian (1820 - 2700 µg/L, Woldemariam and Chandravanshi, 2011), and Cretan wines (up to 3100 µg/L, Galani-Nikolakaki et al., 2002).

Nickel was determined in only four out of the 24 analysed wines, with an average concentration of 259 µg/L. The wines from Stolac and Čitluk did not contain Ni in concentrations above the limit of detection of the applied analytical method. However, its concentrations in two red wines from Trebinje (R-T1) and Ljubuški (R-L1) were four nearly five times higher than the maximum acceptable limit for Ni in wine (100 µg/L) that was previously set in some national regulations (Croatian Government, 1996). At the same time the average concentration of Ni found in four Herzegovinian wines was well above average concentrations of Ni referred for some Croatian (45 µg/L, Bukovčan et al., 2009), Spanish (29 and 38 µg/L for wines from two regions, García-Rodríguez et al., 2011), Turkish (7 - 118 µg/L, Sen and Tokatli, 2014), French (5 - 88 µg/L, Teissèdre et al., 1998a), Ethiopian (180 - 200 µg/L, Woldemariam and Chandravanshi, 2011), Italian (10 – 60 µg/L, Volpe et al., 2009), Greek (16 µg/L, Lazos and Alexakis, 1989) and Romanian wines (8 - 94 µg/L, Voica et al., 2009). In an extensive review of the concentrations of metals in wines from several countries, Pohl (2007) cited the maximum concentrations of Ni up to 500 µg/L in Greek, and up to 200 µg/L in Jordanian wines. Galani-Nikolakaki et al. (2002) reported up to 2300 µg/L of Ni in Cretan wines, indicating stainless steel wine vessels as its primary source. Vanadium in concentrations above the detection limit of the applied analytical method was determined in six white and five red wines, with an average concentration of 17 µg/L. Average concentrations of V were slightly higher in white (21 µg/L) than in the red wines (12 µg/L). Vanadium was found in only one wine from the Trebinje locality. Regardless of the health risks attributed to this metal (Hague et al., 2008), the OIV or, to our knowledge, other institutions have not regulated maximum allowed concentrations of V in wines. The concentration of V in the analysed Herzegovinian wines were comparable to those referred for some French and Californian wines (7 - 90 µg/L in red and 7 - 44 µg/L in white wines, Teissèdre et al., 1998b), and Italian wines (from 13 to 37 µg/L, Galgano et al., 2008). It was slightly lower than that referred for some Spanish wines (44 and 51 µg/L for wines from the two regions, García-Rodríguez et al., 2011).

Chromium was found in only two white and three red wines, with an average concentration of 417 µg/L. The average concentration of Cr in red wines (649 µg/L) was more than nine times higher than its average concentration in two white wines (71 µg/L). The older regional regulations (Croatia) set the maximum allowed concentration of Cr in wine at 100 µg/L. Therefore, the mentioned wines contained Cr at concentrations of more than four to more than seven times higher than that maximum. Much lower concentrations of Cr were reported for some Italian (15 - 20 µg/L, Galgano et al., 2008), Croatian (16 µg/L, Bukovčan et al., 2009), Slovenian (17 µg/L, Kristl et al., 2003), Turkish (5 - 94 µg/L, Sen and Tokatli, 2014), Ethiopian (75 - 192 µg/L, Woldemariam and Chandravanshi, 2011), Spanish (20 µg/L, Lendinez et al., 1998), Greek (99 µg/L, Lazos and Alexakis, 1989), and Argentinian wines (up to 6 µg/L, Lara et al., 2005). The concentrations of Cr comparable to those in the analysed Herzegovinian wines were found in some Romanian wines (70 to 400 µg/L, Voica et al., 2009).

Concentrations of metals and wine locality of origin

In order to obtain an overview of the possible classification of wines by the content of metals and locality of origin, the principal component analysis (PCA) was applied. When the data matrix was subjected to PCA, three significant principal components (PCs) were found. They explained 82.1% of the data variability. The first component (PC_1) was directly correlated with the concentrations of Pb, Cu, and Zn, and the second (PC_2) was correlated with the concentrations of Ni and Cr (Fig. 2-a). The third component (PC_3) was related to the content of Mn (Fig. 2-b).

On Fig. 2, arbitrary ellipsoids encircle wines with common contents of metals. The wines could be divided into three groups on the PCA scatter plot according to the locality and the colour of wine. The first group contains wines with higher contents of Cu, Zn, and Pb. One red and all three white wines from Stolac were separated from the rest by their higher concentrations of Cu, Zn, and Pb which contributed to PC1. Contents of Ni and Cr were a factor of differentiation for the red wines (R-S1, R-L1, R-T1) obtained from three different localities: Stolac, Ljubuski and Trebinje. Wines from Čitluk did not contain these metals. Finally, two wines from Čitluk (R-C2, W-C2), and one wine from Stolac (R-S3) were separated in the third group due to higher contents of Mn than in other wines.

With the partial exception of wines originating from Stolac, this study did not find a strong linkage of the regional origin and the concentrations of the seven metals determined in them. It was also not possible to find any firmconnection between the concentrations of metals in wines from the same varieties originating from different micro locations. With perhaps one exception (micro locality Vionica, wines Žilavka W-C1 and Blatina R-C1), there were not obvious links between the concentration of metals in wines from different varieties originating from the same micro locations. This study indicates that different concentrations of the seven determined metals in the analysed Herzegovinian wines were rather influenced by different viticultural and oenological practices than its locality of origin.

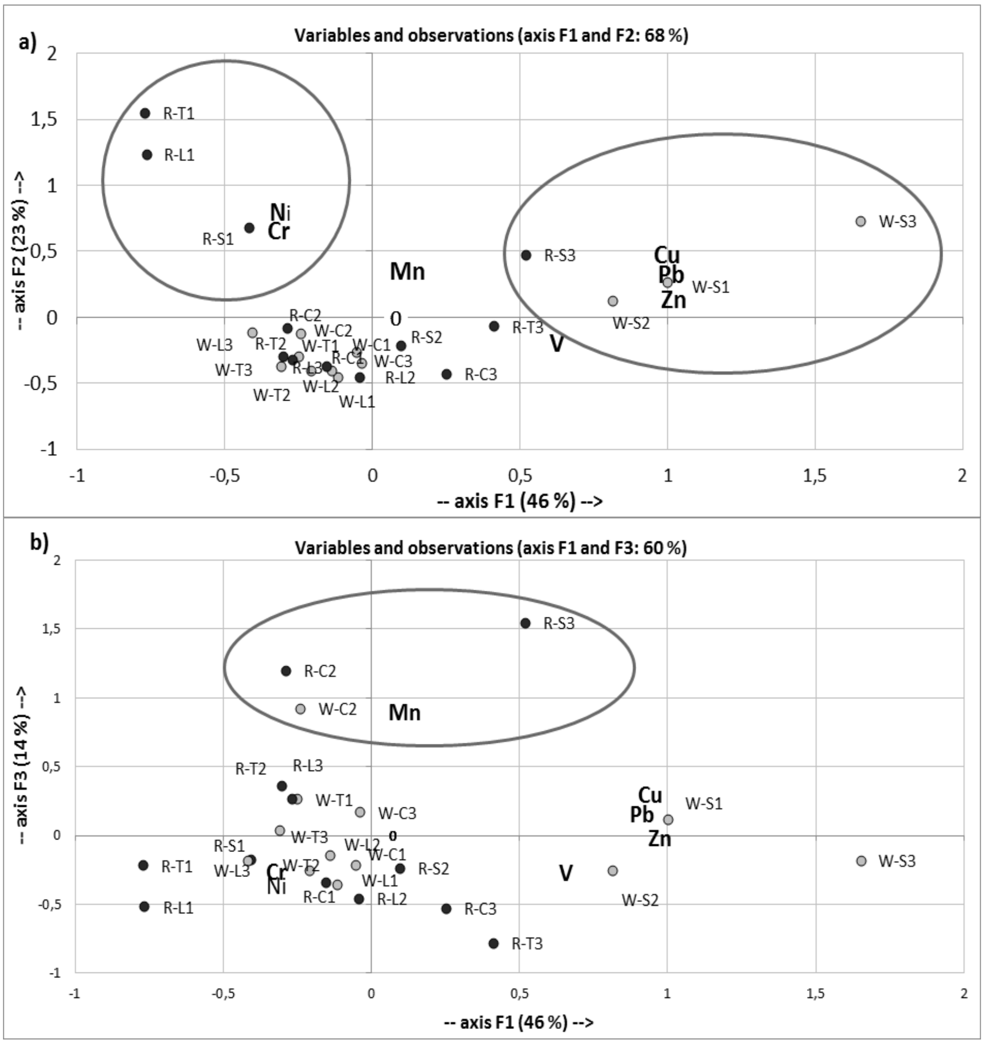

Fig. 2. PCA biplot over PC1-PC2 (a) and PC1-PC3 (b) of the content of metals (Cu, Pb, Zn, Mn, V, Cr, and Ni) and overall positioning of 24 wine samples

Conclusions

The study for the first time presented concentrations of Pb, Cu, Zn, Mn, Ni, V, and Cr in Herzegovinian white and red wines originating from the Čitluk, Ljubuški, Stolac and Trebinje localities. None of the 24 analysed wines contained all seven measured metals, with Zn and Mn being the only metals determined in all wines. Although the concentrations of metals in wines in most cases were below their regulated maximum acceptable limits, unacceptably high concentrations of Cu, Cr, Ni and Pb were found in a small number of wines. With the partial exception of white wines from the Stolac locality, which, compared to other wines, contained remarkably higher concentrations of Cu, Pb, and Zn, the PCA could not confirm links between the localities of grape growingfor wine production and concentrations of analysed metals in the wines. It can be assumed that the found distinctly different concentrations of the measured metals in the analysed wines were influenced by different viticultural and oenological practices rather than soil and other environmental conditions on the localities where grapes for wine production were grown. Furthermore extended researches should concentrate on possible sources of contamination of Herzegovinian wines with metals in the entire chain from the vineyard to the bottle.

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