Influence of Applied Phytosanitary Treatments and Climatic Crop Year on Zinc Content in Wines from Tohani Vineyard

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Metallic ions present a great importance in oenological practice and usually are present in wines in levels that are not hazardous. Among all metallic ions, zinc presents a great interest because may cause the persistence of the wine sour taste and by the side of Al, Cu, Fe and Ni, contribute to the haze formation and the change of color. The present study was focused on measuring the concentration levels of mobile zinc from vineyard soil before and after phytosanitary treatments and zinc content from white (Feteasca Alba - FA, Riesling Italian - RI, Sauvignon Blanc - SB, Tamaioasa Româneasca - TR), rose (Busuioaca de Bohotin - BB) and red (Feteasca Neagra - FN) wines within the wine-growing Tohani area, Romania. Other objective was to investigate of the influence of crop year and variety on zinc levels found in wine samples. Mobile zinc content for all analyzed soil samples is low (<1.5 mg/kg). Analyses indicated that zinc content found in wines was below 5 mg/L, limit set by Organisation Internationale of Vine and Wine (OIV). Also, it was found that red wines contain zinc in higher concentrations than white ones.

Keywords: phytosanitary treatments, soil, vineyard, zinc, wine

Wine is the most consumed beverage all over the world and it has been estimated that the medicinal use of wine dates back to 2200 BC [1]. Moderate wine consumption it is associated with antioxidant effects, allows cholesterol to be cleared before it is deposited in undesired locations in the body, decreases cardiovascular mortality and there are evidences that may decrease the risk of several types of cancer [1,2].

Wine it is a very complex product that contains water, alcohols (ethanol, methanol, glycerol, 2,3-butanediol), organic acids (tartaric, malic, citric, succinic, mucic), esthers (ethyl acetate), aldehydes (ethanal and traces of propanal, hexanal), ketones, sugars (glucose, galactose, fructose, trehalose), pectic substances, aminoacids, flavonoids, anthocyanins, tannins, terpene compounds, bioamines, vitamins, inorganic species [3-5].

Although inorganic species represent a small percentage of wine total composition, they fulfill important roles in winemaking processes and influence the quality of the final product [6].

Metals present in wine reflect the average composition of vineyard soils and are very good indicators of wine origin and may be used as guarantees for its authenticity [7]. The mineral profile of wines is a fingerprint that may classify the wines according to their geographical origin [8].

The presence of metals in wine was intensively monitored [3,9-13] because their levels at different stages of winemaking processes are of great concern being correlated either with some toxicological issues or with decreasing of wine quality often associated with fraudulent practices [4].

Mineral composition of wines depends on soil characteristics (metals and nutritive species contents, physical properties), phytosanitary treatments (Bordeaux mixture, zinc thiocarbamates), oenological practices, environmental contamination, technical equipment used in the wineries or fraudulent addition of forbidden chemicals [3,14].

Among all metallic ions, zinc presents a great interest, being involved in plant growth. It fulfills a major role in the auxin metabolism, protein synthesis, seed formation and it is a promoter for RNA synthesis [15]. Withal, zinc act as catalysts of oxidation reactions and promoters of some enzymes [11].

In wine, zinc is encountered in small concentrations that usually range between 0.14-4 mg/L [4]. Higher concentrations may appear due to environmental contamination [16], use of zinc containers during wine processing and aging stages [9] or use of zinc-based fungicides [9].

Literature survey regarding zinc content in wines revealed that in most cases (table 8) found contents were below limit set by Organisation Internationale of Vine and Wine (OIV) (5 mg/L), excepting some studies [9] when, due to a certain degree of contamination in winery, the zinc level was found 5.5 mg/L.

Decrease of zinc levels in wine can be achieved using potassium ferrocyanide: 2.5 mg/L Zn in wine will decrease to 1.0 mg/L and 0.2 mg/L after treating wine with 50 mg/L and 90 mg/L potassium ferrocyanide, respectively [4].

There are studies that pointed out that zinc causes the persistence of the wine sour taste [17]. Zn by the side of Al, Cu, Fe and Ni, contribute to the haze formation and the change of color due to complexation reaction with anthocyanins and tannins [17].

Given the fact that metallic ions are an outstanding approach to identify the geographical origin, determine wine stability and quality, the analysis of elemental concentration in wines becomes an important demand.

Having in view the importance of zinc and its implications in vine plants and wines it turns out to be interesting to study and fulfill several objectives concerning zinc contents from soil and wines from Tohani area, Romania, as it follows: **(a)** assessment of mobile zinc content in soil samples collected from 0-20 and 20-40 cm depths before and after phytosanitary treatments; **(b)** investigation of correlation between mobile Zn content and soil reaction (*p*H) for 0-20 and 20-40 cm depths; **(c)** assessment of zinc content in white, rose and red wines produced by Tohani vineyard; **(d)** investigation of the

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influence of crop year and variety on zinc levels found in wine samples.

Experimental part

Description of area

Tohani is a locality in Prahova County, Romania. From geographical point of view, Tohani is located in a downy area covered by the Curvature Sub-Carpathians and it became known over time because of the important wine-growing areas (fig. 1).

Placed in the heart of Dealu Mare vineyard, Tohani area is a well-known place on the already famous *wine road.* It is also the beneficiary of ideal conditions for grapes and vine harvesting, being surrounded by a favorable microclimate, that allows the grapes to ripen 10 days earlier than the vineyards in the neighborhood. It is notorious that Vineyard *Great Hill,* called *Motherland of Red Wines* in Southern Carpathians, is the Romanian wine area with climatic conditions very similar to the Bordeaux region [18]. The climate is temperate continental, with cold winters and hot summers. The average annual temperature is 11.3 ^{o}C and the recorded mean annual precipitation is 642 mm.

In Tohani area, the most common soils are Cambisol, Luvisol and Regosol and they are characterized by moderate natural fertility.

Phytosanitary treatments

For pest and disease control, in vineyard were applied phytosanitary treatments by spraying the vine leaves.

Analytical procedures

Before analysis, the samples were carefully prepared in order to avoid chemical and physical interactions. All analyses were performed in triplicate and it was reported the mean value.

Soil samples

Soil samples were collected from Tohani vineyards plots from two depths 0-20 cm and 20-40 cm. It was determined the value of *p*H (soil reaction) through potentiometric method, in an aqueous suspension, 1:2.5 (w/v). The mobile form of zinc was quantified by FAAS means (analytical line 213.9 nm) after performing an extraction according to method developed by Lacatusu et. al [19] and described in detail in a previous paper [13].

Wine samples

The analyzed wine samples were produced by Tohani Dealu Mare (table 2) and it were processed according to a method reported by Artimon et al. [20].

Fig 1. Position of Tohani on Romania map (left) and on Prahova County map (right)

Table 1
PHYTOSANITARY TREATMENTS

Phytosanitary treatments	Application date	Soil sampling date	Products with active substances
T_1	30.06.2010	19.07.2010	Bifenthrin, copper oxychloride, Dimethomorph, Mancozeb, Mefenoxam, Metiram, Propineb, sulphur
T_2	20.07.2010	20.07.2010	α-Cypermethrin, copper hydroxide, Dinocap, Lambda cyhalothrin, Mancozeb, Tebuconazole, sulphur

Table 2
CLASSIFICATION OF ANALYZED WINES

Wine samples		Code	Number of wine samples		
			2009	2010	2011
Fetească Albă	white	FA	4	4	4
Riesling Italian		RI	4	4	4
Sauvignon Blanc		SB	4	4	4
Tămâioasă Românească		TR	4	4	4
Busuioacă de Bohotin	rosé	BB	4	4	4
Fetească Neagră	red	FN	4	4	4

Table 3
USED EQUIPMENT FOR VARIOUS PROCEDURES

Laboratory instruments	Purpose
AAS spectrometer Zeenit 700 (Analytic Jena)	zinc (mobile form)
ELIX 3 system (Millipore)	deionised water
inoLab pH/ION 735 (WTW)	soil pH
microwave Ethos Pro (Milestone)	wine digestion
Simplicity UV system (Millipore)	ultrapure water

Reagents and equipment

All reagents were of analytical grade or better. Laboratory glassware was kept at least 24 h in HNO_3 10% solution. Before use, the glassware was rinsed with ultrapure water.

A stock solution of 1000 ppm zinc provided by Merck was used to prepare the standards for calibration curve. The calibration curve for zinc is linear for the studied range and was plotted by running different concentrations of standard solutions.

Results and discussions

Mobile zinc content in analyzed soil samples

Mobile form of zinc, *p*H values on two sampling depths are presented in table 4.

Literature studies indicate that zinc availability in soil solution is maxim at *p*H=4 and a minim for neutral and basic medium [21,22]. Increase of zinc levels in soil occur with *p*H decrease, the analyzed samples presenting neutral and slightly alkaline reaction for which zinc mobility is lower with no significant differences of *p*H range.

Mobile zinc content is determined by soil sorption complex fraction achieved by exchanging clay mineral fraction and by formation of chelates with humic acids; mobility and bioavailability for plants is correlated with soil reaction, encountering the lowest level at *p*H values higher than 7.0-7.6 [23,24].

Lindsay and Norvell [25] reported a linear correlation between activity of Zn^{+2} ions that dissociate from sorption complex and soil reaction: pZn=2*p*H - 5.7 that arises from $\log(Zn^{2+}) = 5.7 - 2pH$, where $pZn = -\log(Zn^{2+})$. According to this relation it may be concluded that for increase of *p*H with an unit the mobility and accessibility of zinc, expressed as Zn^{+2} activity, decreases of 100 times.

According with those above mentioned, the influence of *p*H on Zn mobilization for 0-20/20-40 cm depth using our analytical results are presented in figure 2 and figure 3.

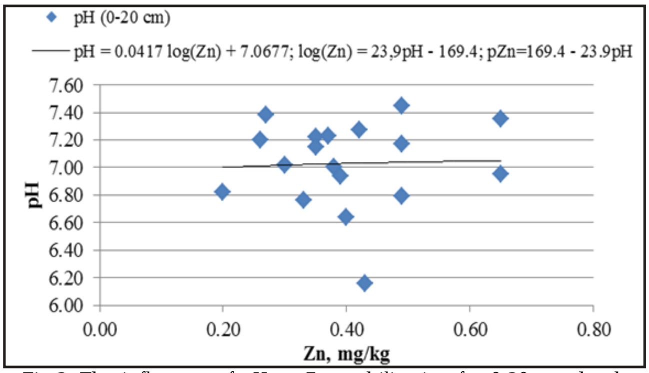

Fig 2. The influence of *p*H on Zn mobilization for 0-20 cm depth

Table 4
MOBILE ZINC CONTENT AND SOIL REACTION FROM SOIL BEFORE (T_0) AND AFTER PHYTOSANITARY TREATMENTS (T_1, T_2)

Soil sample	Treatment	Zn_{mobile}, mg/kg		pH	
		0-20 cm	20-40 cm	0-20 cm	20-40 cm
FA (white)	T_0	0.65	0.18	6.95	6.90
	T_1	0.35	0.28	7.22	7.03
	T_2	0.65	0.51	7.35	7.25
RI (white)	T_0	0.49	0.26	6.79	7.03
	T_1	0.42	0.38	7.27	7.12
	T_2	0.49	0.31	7.45	7.23
SB (white)	T_0	0.20	0.29	6.82	6.97
	T_1	0.35	0.30	7.15	7.21
	T_2	0.27	0.23	7.38	7.30
TR (white)	T_0	0.43	0.21	6.16	5.74
	T_1	0.39	0.20	6.94	6.50
	T_2	0.26	0.21	7.20	7.10
BB (rosé)	T_0	0.33	0.27	6.76	5.59
	T_1	0.38	0.29	7.00	7.13
	T_2	0.37	0.26	7.23	7.33
FN (red)	T_0	0.40	0.31	6.64	6.74
	T_1	0.30	0.27	7.02	7.19
	T_2	0.49	0.32	7.17	6.97

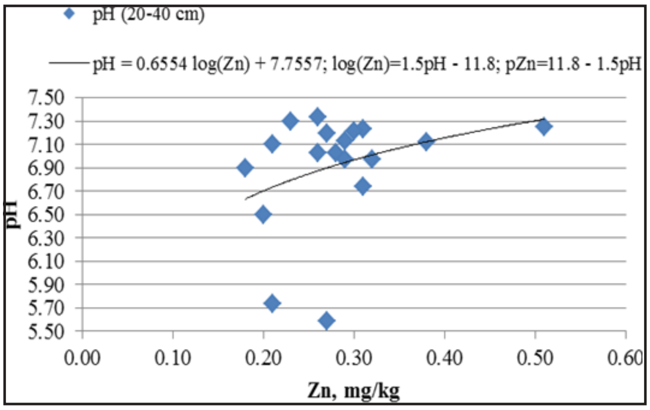

Fig 3. The influence of *p*H on Zn mobilization for 20-40 cm depth

According to Lacatusu et. al [19], mobile zinc content for all analyzed soil samples is low (<1.5 mg/kg).

Zinc content in analyzed wine samples

Zinc concentrations found for each sort of analyzed wine, for each investigated year are presented in table 5.

According to literature [3], red wines contain zinc in higher concentrations than white ones. This is consistent with our present research (table 5). For **SB, FA** and **RI** wines, the obtained results are around twice times lower than those reported by Avram et al. [26] (table 6).

The influence of vine variety on zinc content found in wine samples is significant. Red wine **FN** presents the highest zinc concentrations irrespective of crop year with values of 0.240 mg/L (2010), 0.293 mg/L (2011), 0.317 mg/L with significant differences as against white and rose analyzed wines.

The lowest zinc levels are found for white wine **RI** with values of 0.085 mg/L (2009), 0.066 mg/L (2010) and 0.077 mg/L (2011).

Variance analysis indicates significant differences on zinc accumulation in wines given by crop year (table 7). Years 2009 and 2011 were considered favorable in terms of climate for vine growing, with wine yield by 23% in 2011 higher in comparison with 2010. Disadvantageous and changeable weather in 2010 generated lower wine production by approximately 33% compared to 2009. The year 2010 had a debut with hail and floods, followed by hot weather and as consequence, vine crops were strongly compromised [27].

Applied phytosanitary treatments produced during all three investigated crop years different zinc accumulations with significant differences such as in 2009 and 2011 were

Table 5
ZINC CONTENT IN ANALYZED WINE SAMPLES

Wine	Year	Zn, mg/L (min-max)	X ± SD	CV, %
FA (white)	2009	0.098-0.121	0.113±0.010	9.07
	2010	0.079-0.102	0.091±0.009	10.80
	2011	0.128-0.142	0.135±0.005	4.27
RI (white)	2009	0.078-0.092	0.085±0.006	7.12
	2010	0.058-0.074	0.066±0.006	10.04
	2011	0.069-0.089	0.077±0.008	11.46
SB (white)	2009	0.113-0.131	0.124±0.008	6.48
	2010	0.179-0.193	0.184±0.006	3.25
	2011	0.207-0.253	0.230±0.019	8.38
TR (white)	2009	0.198-0.215	0.206±0.008	3.90
	2010	0.176-0.192	0.184±0.007	4.07
	2011	0.169-0.183	0.175±0.005	3.36
BB (rosé)	2009	0.118-0.134	0.130±0.010	7.78
	2010	0.169-0.182	0.175±0.005	3.13
	2011	0.152-0.173	0.163±0.009	5.83
FN (red)	2009	0.282-0.308	0.293±0.011	3.80
	2010	0.221-0.254	0.240±0.014	5.91
	2011	0.298-0.342	0.317±0.018	5.96
MAL	5 mg/L, according to OIV			

Values are expressed as mean ± standard deviation for n=4; SD=standard deviation; CV=coefficient of variation; MAL - maximum admitted level

Table 6
QUANTIFICATION OF THE ZINC CONTENT IN ANALYZED WINES

Zn, mg/L	white				rosé	red	Samples	% from total
	FA	**RI**	**SB**	**TR**	**BB**	**FN**		
<0.100	4	12	-	-	-	-	16	22.22
0.101-0.200	8	-	8	9	12	-	37	51.38
0.201-0.300	-	-	4	3	-	8	15	20.83
0.301-0.400	-	-	-	-	-	4	4	5.55

Table 7
THE INFLUENCE OF CROP YEAR AND VARIETY ON ZINC LEVELS FOUND IN ANALYZED WINE SAMPLES

Zn, mg/L			
b= Year / a= Variety	b1= 2009	b2=2010	b3=2011
a1= FA (white)	d0.113b	c0.091c	d0.135a
a2= RI (white)	e0.085a	d0.066b	e0.077a
a3= SB (white)	c0.124c	b0.185b	b0.230a
a4= TR (white)	b0.206a	b0.184b	c0.175b
a5= BB (rosé)	c0.130b	b0.175a	c0.163a
a6= FN (red)	a0.293b	a0.240c	a0.317a
[1]B constant A variable: LSD 5%=0.013* mg/L; LSD 1%=0.018 mg/L;LSD 0.1%=0.0246 mg/L [2]A constant B variable: LSD 5%=0.013* mg/L; LSD 1%=0.018 mg/L; LSD 0.1%=0.0244 mg/L			

There were made interpretations by LSD 5% indicated in the table by *
[1]Means with different letters in a column (in front of data) are significant different.
[2] Means with different letters in a row (in back of data) are significant different.

Table 8
OVERVIEW ON ZINC CONTENT FROM WINES ORIGINATING FROM DIFFERENT COUNTRIES

Country	White wine (mg/L)	Rosé wine (mg/L)	Red wine (mg/L)	Ref
Argentina	0.095	-	0.110	[28]
Austria	0.37-0.70	-	-	[29]
Brazil			0.15-1.64	[6]
Bulgaria	-	-	1.26	[30]
Canada	0.7	-	0.8	[31]
Czech Republic	0.78	-	-	[29]
	0.290-0.540		0.470-1.000	[32]
Chile	0.28-1.49	-	0.21-1.63	[33]
Croatia	-	-	0.266-2.434	[34]
	0.102-3.07	-	-	[35]
	0.330-0.691	-	-	[36]
Ethiopia	1.82; 2.40	-	2.14; 2.70	[37]
France	-	-	3.06	[30]
Georgia	0.69-0.86	-	0.53-0.94	[29]
Greece	-	-	0.652; 0.978	[38]
Hungary	-	-	2.08	[30]
Italy	0.36-0.60	-	-	[29]
	-	-	0.56-0.72	[39]
	0.2-3.7	-	-	[40]
Morroco	0.330-0.691		0.563-0.771	[41]
Romania	0.178-1.442	-	0.057-1.004	[10]
	0.409 (SB)* ;0.256 (FA)* ; 0.283 (RI)*	-	-	[26]
Spain	-	-	1.61	[30]
	-	-	0.224-0.455	[11]
Switzerland	0.56-0.96	-	0.68	[29]
Turkey	-	-	1.58-5.07	[42]
	2.099	-	0.389	[43]
NA#	-	0.514	-	[44]
	-	0.5-1.5	-	[45]

*SB - Sauvignon Blanc; FA - Feteasca Alba; RI - Riesling Italian; #NA- information about wines provenance is not available.

found higher concentrations in comparison with 2010. In conclusion, years those are climatologically favorable for wine production (good quality and high yield) induce, under the same treatment conditions, a better zinc absorption in grapes that is encountered in obtained wine.

A comparative presentation of zinc levels found white rose and red wines from different countries is depicted in table 6.

Conclusions

Since zinc presents a great interest in wine technology because may cause the persistence of the wine sour taste and by the side of Al, Cu, Fe and Ni, contribute to the haze formation and the change of color, we developed a study with the aim of achieving the zinc content (mobile form) from vineyard soil before and after phytosanitary treatments and zinc content from white, rose and red wines within the wine-growing Tohani area, Romania.

The results of the research may include the following specific findings:

Mobile zinc content for all analyzed soil samples is low (<1.5 mg/kg).

All analyzed wine samples contain zinc much lower than 5 mg/L, limit set by OIV.

Red wines contain zinc in higher concentrations than white ones.

The influence of vine variety on zinc content found in wine samples is significant. Red wine **FN** presents the highest zinc concentrations irrespective of crop year with values of 0.240 mg/L (2010), 0.293 mg/L (2011), 0.317 mg/L with significant differences as against white and rosé analyzed wines.

The lowest zinc levels are found for white wine **RI** with values of 0.085 mg/L (2009), 0.066 mg/L (2010) and 0.077 mg/L (2011).

Applied phytosanitary treatments produced during all three investigated crop years different zinc accumulations with significant differences such as in 2009 and 2011 were found higher concentrations in comparison with 2010.

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