Impact of Soil Properties on Variability of Iron Content in Wines from Tohani Vineyard

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Knowledge of metal content from wines is crucial for winemakers and consumers, as well. With respect to quality and safety of wine, because of nutritional value or toxicological effects of metals in wine, analysis of metals present a particular interest. The aim of the present research was to evaluate the content of mobile iron from vineyard soil, total iron from grapes and wines from Tohani area, Romania. Other objectives were to correlate the mobile iron content with soil pH values, active CaCO₂ and to study the influence of crop year and variety on iron content from grapes and wines (Feteascã Albã, Riesling Italian, Sauvignon Blanc, Tãmâioasã Româneascã, Busuioacã de Bohotin and Feteascã Neagrã). All wine samples contain iron at levels much lower than concentrations that would produce undesirable effects on wine quality (cloudiness, color change), the highest value being found for rosé wine Busuioacã de Bohotin (2.642 mg/L).

Keywords: vineyard, grape, wine, iron

Wine has been produced by people from ancient times and even today it is not clear in which part of the world it was produced for the first time [1]. Nowadays, wine occupies an important place in many cultures and is a beverage commonly consumed worldwide being an

important source of minerals for humans.

Wine composition is varied and depends by soil characteristics, phytosanitary treatments, wine-making techniques, fraudulent addition of forbidden chemicals, preservation and bottling [2]. Notwithstanding, some species are always found in wine: water, alcohols (ethanol, methanol, glycerol, 2,3-buthanediol), 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 anions and cations [2-4].

The concentrations of metallic ions in wine have a great importance since their presence may influence the taste properties, color, aroma of wine (Fe, Cu, Al, Zn), may have essential role for human health (K, Ca, Mg, Fe, Cu, Mn, Zn) or contrariwise, may pose health risks and undesirable

effects for consumers (Pb, Cd, As) [5].

Moreover, the differentiation of wines can be carried out using major, trace and ultratrace elements [6]. In literature, there are extensive studies that present the distinction of wine according to their origin [6-11] and the mean adopted to discriminate wines coming from different geographical origins is elemental profile, a chemical descriptor used to classify the wines according to their provenance [6].

The elemental profile may be achieved using various analytical techniques, such as: flame atomic absorption spectrometry (FAAS) [12-14], electrothermal atomic absorption spectrometry (ETAAS) [15], hydride generation atomic absorption spectrometry (HGAAS) [16,17], inductively coupled plasma-mass spectrometry (ICP-MS) [8-10,18,19], inductively coupled plasma optical emission spectrometry (ICP-AES) [10,11,19,20], total reflection X-ray fluorescence spectrometry (TXRF) [5, 21], square-wave anodic stripping voltametry (SWASV) [22].

Among all metallic ions, iron is present in wine in concentration that ranges between 0.5 and 25 mg/L [23]

and from that up to 5 mg/L appear from grapes [3]. Iron is found in soluble complexes with organic acids, aminoacids and polyphenols as ferrous (Fe^{+2}) and ferric (Fe^{+3}) ions [3,24].

Iron presents a great importance for wine technology because in excess, it may produce cloudiness or color change (browning). This unwanted process occurs when wine is aerated and ferrous ions are oxidized to ferric ions leading to blue casse (precipitation of coloring matter) or white casse (cloudiness in the case of white wines) [23]. It has been proven that the risk of casse is not possible to be predicted only on the basis of total iron content, because some wines become turbid when iron is about 6-8 mg/L, whereas others remain clear even at concentrations of 25 mg/L [3]. Lazos et al. [25] stated that iron levels of 7-10 mg/L may cause cloudiness or color change.

Cacho et al. [26] reported that manganese and iron ions are involved in chemical processes with acetaldehyde, the latter being the catalyst of acetaldehyde combination with

phenolic compounds.

Among the techniques that are involved in decrease of excessive iron content in wines are the treatments with citric acid and arabic gum, ascorbic acid, calcium phytate. The most popular method suppose the addition of potassium ferrocyanide (1 mg of iron requires 6-9 mg of potassium ferrocyanide) but there are many precautions concerning its use, because it may happen the breakdown of potassium ferrocyanide in wine forming hydrocyanic acid, a very toxic product. That is why in some countries, the winemakers must declare to the authorities their intention to use this treatment [3]. On the other hand, there are researches that describe the use of resins with the aim of decrease of iron content in white wines for reducing the tendency of browning, but the results indicated beside decreased iron level, significant losses in the organoleptic characteristics of the wines [27].

An important constraint concerning iron and its importance in winegrowing technology is its deficiency that produces undesirable effects that are associated with low yields, poor grape quality, low sugar and anthocyanin contents [28]. The main visual effect associated with iron deficiency on plants is chlorosis that appear due to decrease of the chlorophyll and carothenoid levels in leaves

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[28] and this is related with insufficient iron accumulation in leaves or to immobilization into physiologically inactive

forms [29].

Having in view the importance of iron and the diversity of its roles and implications in vine plants and wines it turns out to be interesting to study and fulfill several objectives concerning iron contents from soil, grapes and wines from Tohani area, Romania, as it follows: (1) the influence of phytosanitary treatments and sampling depth on mobile iron content from soil, (2) the correlation between mobile iron content and soil reaction (pH), (3) the correlation between mobile iron content and active CaCO₃ from soil, (4) the influence of crop year and variety on iron content from grapes, and (5) the influence of crop year and variety on iron content from wine.

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-

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 [30]. The climate is temperate continental, with cold winters and hot summers. The average annual temperature is 11.3°C and the recorded mean annual precipitation is 642

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.

First treatment (T₁), applied at 30.06.2010, consisted in a mixture of comercial products that contain as active substance the following: Bifentrin, copper oxychloride, Dimetomorph, Mancozeb, Mefenoxam, Metiram, Propineb, sulphur.

The second treatment (T_a) was applied at 20.07.2010 and was formulated using comercial products that contained α-Cypermethrin, copper hydroxide, Dinocap, Lambda cihalotrin, Mancozeb, Tebuconazole, sulphur.

Analytical procedures

Before analysis, the samples were carefully prepared in order to avoid chemical and physical interactions.

All analyses were performed in triplicate and the reported value is the average.

Soil samples

Soil samples were collected from Tohani vineyards plots from two depths 0-20 cm and 20-40 cm. The following soil agrochemical analyses were performed:

- soil reaction (pH) was carried out through potentiometric method, in an aqueous suspension, 1:2.5
- active calcium carbonate content after a method described in Handbook of Soil Analysis [31] according to which the soil sample is put in contact with ammonium

oxalate under standard time conditions for shaking. Ammonium oxalate having not reacted with carbonates is then back titrated by manganimetry. Active calcium carbonate is antagonistic to iron and can cause ferric chlorosis.

- mobile iron content

A literature survey presents many extraction methods for mobile forms of metals from soil, sediments and sludge [32-36], but in our country for mobile forms of metals is usually adopted method developed by Lãcãtuou et. al [36].

A soil sample of 10 g was treated with 50 mL extractive solution (EDTA 0.01M and CH₃COONH₄ 1N, at *p*H 7) then it was stirred for 2 h and filtered off [36]. The resulted extract was used to evaluate the mobile form of iron, by FAAS method.

Grape samples

Healthy bunches of grapes were collected at the time of harvest. Grapes were washed with distilled water in order to remove the air-pollutants and dust and then were dried at 70°C. Crucibles with dried sample are calcinated firstly at 250-300°C for organic carbon removal and then the temperature is maintained at 450°C for 8-12 h till grey ashes are obtained. The ashes are treated with HCl 6N and the excess of HCl is evaporated and then the final volume is made up to 50 mL using HCl 0.5 N. This solution is used for iron evaluation through FAAS.

Wine samples

The number of wine samples (white, red, rose) analyzed for the assessment of iron content was achieved as it follows: 6 wine varieties x 4 samples/year x 3 years equals 72 samples. The wine sorts that were analyzed are: Feteascâ Albã (white) (FA), Riesling Italian (white) (RI), Sauvignon Blanc (white) (SB), Tamaioasa Romaneasca (white) (TR), Busuioaca de Bohotin (rose) (BB) and Feteasca Neagra (red) (FN), produced by Tohani Dealu

Wine samples were taken from freshly opened bottles and processed according to a method reported by Artimon et al. [37]. 3 mL of wine have been added in polytetrafluoroethylene (PTFE) vessels, treated with 5 mL HNO, 65% and let for 10 min to react. Then it was added 2 mL H₂O₂ 30% and microwave digested. This procedure helped to eliminate the organic matrix of the wine samples. The solution obtained after digestion was quantitatively transferred in 25 mL volumetric flask and the final volume was made up with distilled water.

Equipment

The pH of soil samples were achieved using ino Lab pH/ ION 735 apparatus.

The iron content was determined using an atomic absorption spectrometer Zeenit 700 from Analytic Jena, in air-acetylene flame and the selected analytical line for iron was 248.3 nm. The deionised water was obtained from ELIX 3 system and the ultrapure water was obtained using Simplicity UV system, provided by Millipore. The samples were digested using a microwave Millestone Ethos Pro apparatus. Grape samples were calcinated using Nabertherm B150 (30-3000°C) oven.

Reagents

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

A stock solution of 1000 ppm iron provided by Merck was used to prepare the standards for calibration curve.

Soil sample	Treatment	Fe _{mobile} , mg/kg		pН		CaCO _{3(active)}	
		0-20 cm	20-40	0-20 cm	20-40	0-20	20-40
			cm		cm	cm	cm
FA	T ₀	8.89	4.70	6.95	6.90	4.25	7.13
ra.	<u>T</u> 1	8.86	7.34	7.22	7.03	-	-
	T ₂	3.93	4.25	7.35	7.25	-	-
	T ₀	5.69	4.06	6.79	7.03	7.19	5.94
RI	T_1	6.01	4.56	7.27	7.12	-	-
	T ₂	3.67	2.45	7.45	7.23	-	-
	T ₀	4.55	7.08	6.82	6.97	6.14	4.35
SB	T ₁	6.65	6.31	7.15	7.21	-	-
	T ₂	3.34	2.68	7.38	7.30	-	-
	T ₀	5.73	4.43	6.16	5.74	5.75	6.25
TR	T ₁	6.42	5.08	6.94	6.50	-	-
	T ₂	3.94	2.44	7.20	7.10	-	-
	T ₀	6.06	4.44	6.76	5.59	5.89	5.44
BB	T ₁	5.48	4.65	7.00	7.13	-	-
	T ₂	3.25	7.16	7.23	7.33	-	-
	T ₀	5.15	4.49	6.64	6.74	6.73	6.07
FN	T_1	6.23	5.16	7.02	7.19	-	-
	T ₂	4.84	4.15	7.17	6.97	-	-

Table 1MOBILE IRON CONTENT, SOIL REACTION AND
ACTIVE CACO $_3$ FROM SOIL BEFORE (T_0) AND
AFTER PHYTOSANITARY TREATMENTS (T_1 , T_2)

 Table 2

 THE INFLUENCE OF PHYTOSANITARY TREATMENTS AND SAMPLING DEPTH ON MOBILE IRON CONTENT FROM SOIL

			Fe mobile (mg/kg)	
•• • •	l [Treatments		
Variety	a\b	b1=T0	b2=T1	b3=T2
FA	a1=0-20cm	a8.89a	a8.86a	b3.93b
	a2= 20-40cm	b4.70b	b7.34a	a4.25c
B constant A variable: DL 5%=0.2 A constant B variable: DL 5%=0.3	25*mg/kg; DL 1%=0.36 mg/kg; DL 0.19 31* mg/kg; DL 1%=0.44 mg/kg; DL 0.19	6=0.51 mg/kg 6=0.62 mg/kg		
RI	a1=0-20cm	a5.69a	a6.01a	a3.67b
	a2= 20-40cm	b4.06b	b4.56a	b2.45c
B constant A variable: DL 5%=0.4 A constant B variable: DL 5%=0.4	40*mg/kg ; DL 1%=0.58 mg/kg; DL 0.19 46* mg/kg; DL 1%=0.65 mg/kg; DL 0.19	6=0.89 mg/kg 6=0.91 mg/kg		
SB	a1=0-20cm	b4.55b	a6.65a	a3.34c
	a2= 20-40cm	a7.08a	a6.31b	b2.68c
A constant B variable: DL 5%=0.4	19*mg/kg ; DL 1%=0.82 mg/kg; DL 0.19 10* mg/kg; DL 1%=0.56 mg/kg; DL 0.19	6=1.59 mg/kg 6=0.79 mg/kg		
	4 2 2 2	5.501	6.40	
TR	a1=0-20cm	a5.73b	a6.42a	a3.94c
TR	a1=0-20cm a2= 20-40cm	a5.73b b4.43b	a6.42a b5.08a	a3.94c b2.44c
B constant A variable: DL 5%=0.2 A constant B variable: DL 5%=0.3	a2= 20-40cm 28*mg/kg; DL 1%=0.42 mg/kg; DL 0.19 30* mg/kg; DL 1%=0.42 mg/kg; DL 0.19	b4.43b 6=0.71 mg/kg		
B constant A variable: DL 5%=0.2	a2= 20-40cm 28*mg/kg; DL 1%=0.42 mg/kg; DL 0.1% 30* mg/kg; DL 1%=0.42 mg/kg; DL 0.1% a1=0-20cm	b4.43b %=0.71 mg/kg %=0.59 mg/kg a6.06a	b5.08a a5.48b	b2.44c
B constant A variable: DL 5%=0.2 A constant B variable: DL 5%=0.3 BB	a2= 20.40cm 88*mg/kg; DL 1%=0.42 mg/kg; DL 0.19 80* mg/kg; DL 1%=0.42 mg/kg; DL 0.19 a1=0-20cm a2= 20.40cm	b4.43b 6=0.71 mg/kg 6=0.59 mg/kg a6.06a b4.44b	b5.08a	b2.44c
B constant A variable: DL 5%=0.2 A constant B variable: DL 5%=0.3 BB	a2= 20-40cm 28*mg/kg; DL 1%=0.42 mg/kg; DL 0.1% 30* mg/kg; DL 1%=0.42 mg/kg; DL 0.1% a1=0-20cm	b4.43b 6=0.71 mg/kg 6=0.59 mg/kg a6.06a b4.44b	b5.08a a5.48b	b2.44c
B constant A variable: DL 5%=0.2 A constant B variable: DL 5%=0.3 BB	a2= 20.40cm 88*mg/kg; DL 1%=0.42 mg/kg; DL 0.19 80* mg/kg; DL 1%=0.42 mg/kg; DL 0.19 a1=0-20cm a2= 20.40cm	b4.43b 6=0.71 mg/kg 6=0.59 mg/kg a6.06a b4.44b	b5.08a a5.48b	b2.44c

There were made interpretations by DL 5% indicated in the table by

The calibration curve for iron is linear for the studied ranges and was plotted by running different concentrations of standard solutions.

Results and discussions

Mobile form of iron, *pH* values and levels of active CaCO₃ on two sampling depths are presented in table 1.

The influence of phytosanitary treatments and sampling depth on mobile iron content from soil

The ferrous ion and also mono- and bivalent species namely, $\mathrm{Fe}(\mathrm{OH})_2^+$ and $\mathrm{Fe}(\mathrm{OH})^{2+}$ are found on soil adsorption complex, meanwhile ferric ion is strongly retained by soil colloids. The iron concentration available to plants is low and varies between 0-25 mg/kg for Fe^{2+} and 0-5 mg/kg for Fe^{3+} . In soil solution, iron oxides and hydroxides become

more soluble with acidity increasing and at *pH* values over 6.5 the solubility declines [38, 39].

The iron distribution correlated with soil sampling depth indicates superior values for surface horizon (0-20 cm). The exception is given by plots with SB and BB varieties where reverse situation occurred, higher levels of mobile iron being found for 20-40 cm: 7.08 mg/kg and 7.16 mg/kg, respectively. This is due to strongly acidic soil reaction (4.35), moderately acidic (5.44), respectively [40].

The influence of phytosanitary treatments on mobile iron from soil are significant and are generated by the effect of these treatments on *pH* value and consequently on bioavailable iron releasing (table 2)

bioavailable iron releasing (table 2).

The soil sampling depth present a significant influence on mobile iron content, the values decreasing with depth increasing and the mobility is influenced by soil acidity. There are not found significant differences on 0-20 and 20-

¹Means 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.

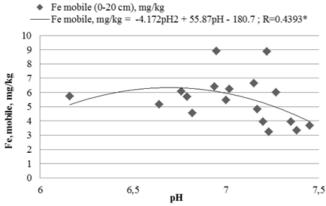


Fig. 1. The correlation between mobile iron content from soil (0-20 cm) and pH

40 cm depths for plot with SB variety for which there are not *p*H fluctuations, with neutral soil reaction (6.81-7.20) and slightly alkaline (7.21-7.50).

The correlation between mobile iron content and soil reaction (pH)

Iron availability is favored by soil acidic *p*H. For soils that were subject of investigation, on the basis of correlation coefficient (0.4393*) we could assume a significant correlation between mobile iron content and soil *p*H on 0-20 cm depth (fig. 1) and no significant correlation on 20-40 cm depth (fig. 2).

The correlation between mobile iron content and active CaCO, from soil

Iron chlorosis in vineyards it may appear due to soil related factors (high soil pH, presence of active CaCO₃, poor soil aeration and soil compaction, low root zone temperature, irrigation with water rich in bicarbonate, low level of soil organic matter and poor biological fertility of soils) or vine related factors (pathogen infection, excessive fruit yield the previous year, damages to the root system) [41]

Active calcium carbonate content from soils is used to calculate *Chlorotic Power Index* which indicates iron deficiency induced by excessive amounts of active calcium carbonate. Soils with active calcium carbonate levels higher than 6-7% may lead to chlorosis [39].

Regarding analysed soils it has been found that the influence of active calcium carbonate content on mobile iron content is very significant for 0-20 cm (fig. 3) and 20-

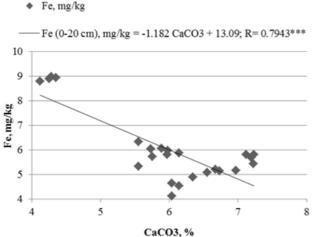
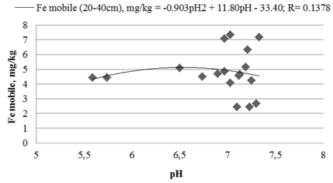


Fig. 3. The correlation between mobile iron content and active CaCO₃ from soil (0-20 cm)



Fe mobile (20-40cm), mg/kg

Fig. 2. The correlation between mobile iron content from soil (20-40 cm) and pH

40 cm (fig. 4) with correlation coefficients of 0.7943*** and 0.6942***, respectively.

The influence of crop year and variety on iron content from granes

grapes
Sofo et al. [42] found that iron content in grape was greater in irrigated treatment (0.24 mg/kg) related with treatment without irrigation (0.064 mg/kg), confirming that low humidity of soil can increase grape and wine quality. This statement was made on the basis of known effect of iron excess in wine that could generate wine turbidity and can delay fermentation during winemaking.

Iron concentration in white grapes found by Orescanin et al. [43] was 0.019 mg/kg, meanwhile in red grapes iron level was 0.142 mg/kg.

The influence of variety on iron content from grapes is significant for majority of monitored varieties (table 3). There are not significant differences between SB and FA in year 2009. In crop year 2010, there are no significant differences between varieties SB and FN and between TR, BB, RI and FA. Also, in year 2011 there are no significant differences for SB and BB, for RI, FA and FN with significant differences as against TR.

In year 2009, the highest levels of iron are found for grape varieties SB (0.185 mg/kg), FA (0.176 mg/kg) and FN (0.162 mg/kg) and this could be a consequence of the rainfall and soil humidity that favored iron mobility.

The most significant differences given by crop year are evidenced for 2009, a year with precipitation that may be considered as yearly average value for this region in comparison with 2010 and 2011. The year 2011 is positioned on 10th place in the top of the warmest years of this century.

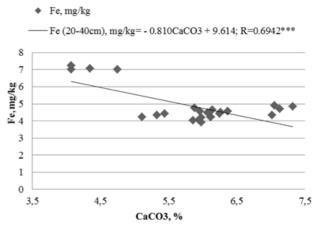


Fig. 4. The correlation between mobile iron content and active $CaCO_{\circ}$ from soil (20-40 cm)

a=variety\b= year	Fe (mg/kg)				
	Year				
Variety	b1=2009	b2=2010	b3=2011		
a1= FA	a0.176a	b0.095c	a0.153b		
a2= RI	d0.116b	b0.085c	a0.143a		
a3= SB	a0.185a	a0.124b	b0.135b		
a4= TR	c0.135a	60.097b	c0.074c		
a5= BB	e0.054c	60.097b	b0.132a		
a6= FN	b0 162a	a0 132b	a0 142b		

¹B constant A variable: DL 5%=0.017*mg/kg ; DL 1%=0.024 mg/kg; DL 0.1%=0.032 mg/kg

There were made interpretations by DL 5% indicated in the table by *

¹Means 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.

Year Fe, mg/L (min-max) $X \pm SD$ 2009 1.278-1.406 1.347±0.058 4.35 FA (white) 2010 1.398-1.560 1.475±0.067 4.57 2011 1.385-1.554 1.474±0.075 5.11 2009 1.213-1.296 1.258±0.038 3.021 RI (white) 13.98 2010 0.968-1.297 1.093±0.152 1.333±0.100 2011 1.197-1.422 7.55 1.737±0.061 2009 1.662-1.812 3.52 SB (white) 2010 1.887-2.084 1.960±0.086 4.39 2011 1.952-2.186 2.066±0.103 5.00 0.989±0.061 2009 0.925-1.065 6.23 TR (white) 2010 0.893-0.964 0.929±0.031 3.40 2011 0.996-1.242 1.120±0.104 9.31 1.719-2.321 1.998±0.274 13.71 2009 BB (rosé) 2010 2.108-2.452 2.243±0.147 6.55 2011 1.992-2.642 2.360±0.329 13.95 2009 1.618-2.232 1.854±0.265 14.32 FN (red) 1.921-2.302 2010 2.105±0.169 8.04 2.023-2.542 2.324±0.221 2011 9.54

 Table 4

 IRON CONTENT IN ANALYZED WINE SAMPLES

Table 3THE INFLUENCE OF CROP YEAR AND VARIETY ON IRON CONTENT FROM GRAPES

Values are expressed as mean ± standard deviation for n=4; SD=standard deviation; CV=coefficient of variation.

Country	White wine	Rosé wine	Red wine	Reference
Argentina	0.65	-	0.60	[47]
Australia	0.1-4.0	-	-	[48]
Brazil	-	-	1.10-6.34	[49]
	0.97-2.84	-	2.33-5.62	[23]
Bulgary	-	-	6.41	[50]
Croatia	2.53-9.66	-	2.14-6.61	[51]
Czech Republic	2.3-3.5	-	1.8-4.6	[10]
Estonia	-	-	0.10-0.13	[52]
France	-	-	5.98	[50]
Grecia	0.70-7.30	1.95-5.60	0.75-5.70	[25]
Hungary	-	-	9.47	[50]
Italy	-	-	2.60-3.92	[8]
	-	5.14-10.15	0.86-9.62	[45]
Morocco	-	-	2.27-4.29	[53]
Portugal	1.2-9.0	-	4.0-5.5	[54]
Romania	-	-	16.8-20.7	[55]
	5.11#	-	-	[56]
	0.29-2.602	-	-	[19]
	-	-	4.67	[50]
Spain	3.9*	-	4.4*	[57]
	4.1**		3.3**	
	-	2.64-10.00	2.38-7.12	[46]
		2.37-9.34	1.84-9.41	
Turkey	-	-	9.14-29.64	[20]
	0.31-1.27		0.59-5.79	[15]

Table 5
OVERVIEW ON
IRON CONTENT
FROM WINES
ORIGINATING
ROM DIFFERENT
COUNTRIES

²A constant B variable: DL 5%=0.019* mg/kg; DL 1%=0.026 mg/kg; DL 0.1%=0.034 mg/kg

^{*}Tamaioasa Romanească variety; *wines from La Gomera Island; **wines from Fuerteventura Island

 Table 6

 THE INFLUENCE OF CROP YEAR AND VARIETY ON IRON CONTENT FROM WINE

a=variety\b= year	Fe (mg/L)				
	Year				
Variety	b1=2009	b2=2010	b3=2011		
al=FA	c1.347a	c1.475a	c1.474a		
a2= RI	c1.258a	d1.094b	c1.334a		
a3= SB	b1.738b	b1.961a	b2.066a		
a4= TR	c0.989a	d0.929a	d1.120a		
a5= BB	a1.999b	a2.244a	a2.360a		
a6= FN	a1.854c	a2.106b	a2.325a		
¹ B constant A variable: DL 5%=0.199*mg/L; DL 1%=0.270 mg/L; DL 0.1%=0.364 mg/L ² A constant B variable: DL 5%=0.201* mg/L; DL 1%=0.270 mg/L; DL 0.1%=0.355 mg/L					

There were made interpretations by DL 5% indicated in the table by *

The influence of crop year and variety on iron content from wine

In the last years, with the increasing use of stainless steel units in wineries it has been observed that the levels of iron in wine decreased and in most cases, therefore the wines contain iron up to 5 mg/L [3,44]. In our investigation, the highest iron content was found in the case of rosé wine (BB, year 2011) (2.642 mg/L), value lower than those reported for rosé wines from Greece [25], Italy [45] and Spain [46]. Also, analyzed red wines contain higher levels of iron than white ones, situation reported also by Alkis et al. [15] for Turkish wines.

Iron found contents in white (FA, RI, SB, TR), rose (BB) and red (FN) wines are presented in table 4 meanwhile, for comparison, an overview of literature data concerning iron content in wines is presented in table 5.

Statistic analysis of the results indicates significant differences given by the variety on the iron content from wine and as consequently, the iron accumulation is variety dependent (table 6). There are no significant differences generated by crop year on iron content for majority of variants; the differences that still appear are preponderant for year 2009 in comparison with 2010 and 2011 that are climatologically alike.

The highest values of iron content (as average) were found for BB, FN and SB wines in all three studied years, the highest values being recorded in 2011: 2.360 mg/L, 2.325 mg/L and 2.066 mg/L, respectively.

Conclusions

Since iron plays an important role in wine technology, in excess being a cause of color change and cloudiness, and having in view its roles for vine plants, we determined the iron content (mobile form) from soil, grapes and wines from Tohani area, Romania. Other objective was to correlate the mobile iron content with soil pH values, active ${\rm CaCO}_3$ and to study the influence of crop year and variety on iron content from grapes and wine.

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

- the influence of phytosanitary treatments on mobile iron from soil are significant and are generated by the effect of these treatments on *pH* value and consequently on bioavailable iron releasing.;
- The soil sampling depth present a significant influence on the mobile iron content, the values decreasing with depth increasing and the mobility is influenced by soil acidity;
- on the basis of correlation coefficient (0.4393*) there is a significant correlation between mobile iron content

and soil *p*H on 0-20 cm depth and no significant correlation on 20-40 cm depth;

- the influence of active calcium carbonate content on mobile iron content from soil is very significant for 0-20 cm depth and 20-40 cm depth with correlation coefficients of 0.7943*** and 0.6942***, respectively;
- in year 2009, the highest levels of iron (as average) are found for grape varieties SB (0.185 mg/kg), FA (0.176 mg/kg) and FN (0.162 mg/kg) and this could be a consequence of the rainfall and soil humidity that favored iron mobility;
- in the case of analyzed wines, the highest iron content was found for rosé wine (BB) (2.642 mg/L), value lower than those reported in literature for rosé wines. Also, it was found that red wines contain higher levels of iron than white ones;
- there are no significant differences generated by crop year on wine iron content for majority of variants; the differences that still appear are preponderant for year 2009 in comparison with 2010 and 2011 that are climatologically alike;
- the highest values of iron content (as average) were found for BB, FN and SB wines in all three studied years, the highest values being recorded in 2011: 2.360 mg/L, 2.325 mg/L and 2.066 mg/L, respectively.

References

- 1. STANCU, A., Economics of Agriculture, (62)1, 2015, p.207.
- 2. VOLPE, M.G., LA CARA, F., VOLPE, F., DE MATTIA, A., SERINO V., PETITTO, F., ZAVALLONI, C., LIMONE, F., PELLECCHIA R., DE PRISCO, P.P., DI STASIO, M., Food Chemistry, 117, 2009, p.553.
- 3. RIBEREAU-GAYON P., GLORIES, Y., MAUJEAN, A., DUBORDIEU, D., The Chemistry of Wine Stabilization and Treatments, 2nd Edition, Handbook of Enology, Volume 2, John Wiley & Sons Ltd., 2006.
- 4. GRINDLAY, G., MORA, J., GRAS, L., DE LOOS-VOLLEBREGT, T.C., Analytica Chimica Acta, **691**, 2011, p.18.
- 5. GALANI-NIKOLAKAKI, S., KALLITHRAKAS-KONTOS, N., KATSANOS, A.A., The Science of the Total Environment, **285**, 2002, p.155.
- 6. FABANI, M., ARRUA, R., VAZQUEZ, F., DIAZ, M., BARONI, M., WUNDERLIN, D., Food Chemistry, 119, 2010, p.372.
- 7. PANEQUE, P., ALVAREZ-SOTOMAYOR, M.T., GOMEZ, I., Food Chemistry, 117, 2009, p.302.
- 8. GALGANO, F., FAVATI, F., CARUSO, F., SCARPA, T., PALMA, A., LWT-Food Science and technology, **41**, 2008, p.1808.
- 9. KMENT, P., MIHALJEVIE, M., ETTLER, V., ŠEBEK, O., STRNAD, L., ROHLOVÁ, L., Food Chemistry, **91**, 2005, p.157.
- 10. ŠPERKOVA, J., SUCHANEK, M., Food Chemistry 93, 2005, p.659.
- 11. ALVAREZ, M., MORENO, I.M., PICHARDO, S., CAMEÁN A.M., GONZALEZ, A.G., Food Chemistry, **135**, 2012, p.309.
- 12. ARTIMON, M., TANASE, I.GH., VASILE, G., Revue Roumaine de Chimie, **54(3)**, 2009, p.247.

¹Means 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.

- 13. CALIN, C., SCAETEANU, G., PELE, M., ILIE, L., PANTEA, O., BOMBOS, D., Rev. Chim. (Bucharest), **63**, no. 10, 2012, p.1062.
- 14. PEREZ TRUJILLO, J.P., CONDE, J.E., PEREZ PONT, M.L., CAMARA, J., MAQUES, J.C., Food Chemistry, **124**, 2011, p.533.
- 15. ALKIS, I.M., OZ, S., ATAKOL, A., YILMAZ, N., ERTAN, A., ATAKOL,
- O., Journal of Food Composition and Analysis, **33**, 2014, p.105. 16. SANTOS, S., LAPA, N., ALVES, A., MORAIS, J., MENDES, B., Journal
- of Environmental Science and Health, part B, **48**, 2013, p.364.
- 17. JOS, A., MORENO, A. G., GONZALEZ, A. G., REPETTO, G., CAMEAN, A. M., Talanta, **63(2)**, 2004, p.377.
- 18. CATARINO, S., CURVELO-GARCIA, A.S., DE SOUSA, R.B., Talanta, **70**, 2006, p.1073.
- 19. GEANA, I., IORDACHE, A., IONETE, R., MARINESCU, A., RANCA, A., CULEA, M., Food Chemistry, 138, 2013, p.1125.
- 19. JURADO, J.M., ALCAZAR, A., PALACIOS-MORILLOR, A., DE PABLOS, F., Food Chemistry, **135**, 2012, p.898.
- 20. DEĐIRMENCI KARATAS, D., AYDIN, F., AYDIN, I., KARATAS, H., Czech J. Food Sci., **33**, 2015, p.228.
- 21. PESSANHA, S., CARVAHLO, M.L., BECKER, M., VON BOHLEN, A., Spectrochimica Acta Part B., **65**, 2010, p.504.
- 22. ILLUMINATI, S., ANNIBALDI, A., TRUZZI, C., FINALE, C., SCARPONI, G., Electrochimica Acta, **104**, 2013, p.148
- 23. FERREIRA, S.L.C., FERREIRA, H.S., DE JESUS, R.M., SANTOS, J.V.S., BRANDAO, G.C., SOUZA, A.S., Analytica Chimica Acta, **602**, 2007, p.89.
- POHL, P., Trends in Analytical Chemistry, 26(9), 2007, p.941.
 LAZOS, E.S., ALEXAKIS, A., International Journal of Food Science and Technology, 24, 1989, p.39.
- 26. CACHO J., CASTELLS J.E., ESTEBAN A., LAGUNA B., SAGRISTA N., American Journal of Enology and Viticulture, 1995, 46, 380-384
- 27. BENITEZ, P., CASTRO, R., BAROSSO, C.G., Analytica Chimica Acta, 458, 2002, p.197.
- 28. MEGGIO, F., ZARCO-TEJADA, P.J., NUNEZ, L.C., SEPULCRE-CANTO, G., GONZALEZ M.R., MARTÍN P., Remote Sensing of Environment, 114, 2010, p.1968.
- 29. BARKER, A.V., PILBEAM, D.J., Handbook of Plant Nutrition, Second Edition, Taylor and Francis Group, LLC, 2015.
- 30. OPREA, M.C., Petroleum-Gas University of Ploiesti Bulletin, **LXII** (2), 2010, p.116.
- 31. PANSU, M., GAUTHEYROU, J., Handbook of Soil Analysis-Mineralogical, Organic and Inorganic Methods, Springer Berlin Heidelberg New York, 2006.
- 32. VASILE, G. G., Monitorizarea concentratiilor speciilor metalice mobile din soluri si sedimente antropizate. Trasabilitatea masuratorilor analitice de metale mobile în soluri °i sedimente. Teza de doctorat, Universitatea Bucuresti, Facultatea de Chimie, 2009.
- 33. VASILE, G., CRUCERU, L., PETRE, J., TANASE, I.GH., Rev. Chim. (Bucharest), **58**, 1no. 2, 2007, p.1332.

- 34. VASILE, G., TANASE, I.GH., Revue Romaine de Chimie, **53(11)**, 2008, p.1041.
- 35. ETTLER, V., MIHALJEVIC, J., SEBEK, O., GRYGAR, T., Analytica Chimica Acta **602**, 2007, p.131.
- $36.\,L\tilde{A}C\tilde{A}TU^aU,\,R.,\,KOVACSOVICS,\,B.,\,GATA,\,GH.\,ALEXANDRESCU,\,A.,\,Pub.\,SNRSS\,23B,\,1987,\,p.1.$
- 37. ARTIMON, M., TANASE, I.GH., PELE, M., CAMPEANU, GH., VASILE, G., Roumanian Biotechnological Letters, **13(6)**, 2008, p.4022.
- 38. DAVIDESCU, D., DAVIDESCU, V., LACATUSU, R., Microelemente în agricultură, Ed Academiei RSR, 1988.
- 39. RUSU, M., MARGHITAS, M., OROIAN, I., MIHAIESCU, T., DUMITRAS, A, Tratat de agrochimie, Ed. Ceres, 2005.
- 40. MADJAR, R., Agrochimie Planta si solul, Ed. Invel, 2008.
- 41. TAGLIAVINI, M., ROMBOLA, A.D., European Journal of Agronomy, **15**, 2001, p.71.
- 42. SOFO, A., NUZZO, V., TATARANNI, G., MANFRA, M., DE NISCO, M., SCOPA, A., Journal of Plant Physiology, **169**, 2012, p.1023.
- 43. ORESCANIN, V., KATUNAR, A., KUTLE, A., VALKOVIC, V., Journal of Trace and Microprobe Techniques, **21(1)**, 2003, p.171.
- 44. LI, H., GUO, A., WANG, H., Food Chemistry, 108, 2008, p.1.
- 45. INTERSESSE, F., LAMPARELLI, F., ALLOGGIO, V., Z. Lebensm. Unters. Forsch., 178, 1984, p.272.
- 46. GONZALEZ, M.J., MARTINEZ PARA, M.C., AGUILAR, M.V., Z. Lebensm. Unters. Forsch., **187**, 1988, p.325.
- 47. LARA, R., CERUTTI, S., SALONIA, J.A., OLSINA, R.A., MARTINEZ, L.D., Food and Chemical Toxicology 43, 2005, p.293.
- 48. SAUVAGE, L., FRANK, D., STEARNE, J., MILLIKAN, M.B., Analytica Chimica Acta, 458, 2002, p.223.
- 49. IOCHIMOS DON SANTOS, C.E., MANFREDI DA SILVA, L.R., BOUFLEUR, L.A., DEBASTIANI, R., ALBERICI STEFENON, C., AMARAL, L., YONEAMA, M.L., FERRAZ DIAZ, J., Food Chemistry, **121**, 2010, p.244.
- 50. CZECH, A., MALIK, A., J.Elem.s., 17, 2012, p.191.
- 51. FIKET, Ž., MIKAC, N., KNIEWALD, G., Food Chemistry, **126**, 2011, p.941.
- 52. PEDASTSAAR, P., VAHER, M., HELMJA, K., KULP, K., KALJURAND, M., KARP, K., RAAL, A., KARATHANOS, V., PUSSA, T., Proceedings of the Estonian Academy of Sciences, **63(4)**, 2014, p.444.
- 53. TENORE, G.C., TROISI, J., DI FIORE, R., MANFRA, M., NOVELLINO, E., Food Chemistry, **129**, 2011, p.792.
- 54. VIDIGAL, S., TOTH, I., RANGEL, A., Talanta, 84, 2011, p.1298.
- 55. POIANA M.-A., Scientifical Researches. Agroalimentary Processes and Technologies, **XI(2)**, 2005, p.457.
- 56. CODREANU, M., COTEA, V., NICULAUA, M., COLIBABA, C., LUCHIAN, C., Bulletin UASVM Horticulture, **70(1)**, 2013, p.75.
- 57. PEREZ TRUJILLO, J.P., PEREZ PONT, M.L., CONDE GONZALEZ, E., CyTA-Journal of Food, **9(2)**, 2011, p.135

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