INDUCTIVELY COUPLED PLASMA - MASS SPECTROMETRY (ICP-MS) AND INDUCTIVELY COUPLED PLASMA – OPTICAL EMISSION SPECTROMETRY (IP-OES) ANALYSIS OF ELEMENTS IN MACEDONIAN WINES

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ELEMENTS IN WINE

The knowledge of the mineral composition and content in wine is an **important factor** influencing its **quality** and **nutritional** value.

- ***toxicological point*** of view - harmful elements, such as **Pb**, **As** and **Cd**

- ***nutritional point*** of view - essential elements for the human organism, such as **Ca**, **Cr**, **Co**, **K**, **Se** and **Zn**.

Aim of the work

1. **To analyse the elemental composition of different wines (red, rose and white, from different regions)**

2. **To study the relationship between element concentrations and two variables:**

   -**wine type (white vs. red)**
   - **geographical indication**

applying two techniques, ICP-OES and ICP-MS for analyses.

EXPERIMENTAL

Wine samples

25 wine samples (10 white wines, 14 red wines and 1 rose wine) from vintage 2011

➢**White**: Temjanika, Žilavka, Riesling, Sauvignon Blanc, Smederevka

➢**Rose**: Stanušina Rose

➢ **Red**: Vranec, Stanušina, Merlot, Cabernet Sauvignon, Syrah, Tempranilo, Pinot Noir, Petit Verdot, Sangiovese

EXPERIMENTAL

ICP-OES and ICP-MS operating conditions

Parameter	ICP-OES	ICP-MS
RF Power	1350 W	1350 W
Cooling gas flow	12.5 L min^{-1}	14 L min^{-1}
Auxiliary gas flow	0.6 L min^{-1}	1.3 L min^{-1}
Nebulizer gas flow	0.83 L min^{-1}	0.91 L min^{-1}
Nebulizer	Cross flow	Meinhard Type A
Spray chamber	Scott type	Cyclonic
Integration time	24 s	1000 ms for each m/z, 50 ms dwell time, peak hopping
Replicates	5	4

EXPERIMENTAL

Sample preparation

5 ml wine + 2 ml HNO_3 digested at 240°C

Validation

One wine sample spiked with 10 µg/L multi-element solution consisting of Ag, Au, Be, Bi, Cd, Ce, Co, Cu, Dy, Er, Eu, Ga, Gd, Ge, Ho, La, Lu, Mo, Nd, Pb, Pr, Sm, Tb, Tl, Tm, U, V, Yb, Zr, for the ICP-MS analysis

Recoveries: 93 and 109 %

The procedure was evaluated by analyzing a CRM (trace elements in water, NIST SRM 1643e)

Statistical analysis

ANOVA, Descriptive analysis, Factor analysis and Cluster analysis in order to extract the important information and to represent the pattern of similarity or differences between the studied wines in order to make a conclusion about the possible classification.

RESULTS AND DISCUSSION

- 42 elements quantified in red, rose and white wine

Ag, Al, Au, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cu, Dy, Er, Eu, Fe, Ga, Gd, Ge, Ho, La, Lu, Mg, Mn, Mo, Na, Nd, Ni, P, Pb, Pr, S, Sm, Tb, Ti, Tl, Tm, U, V, Yb, Zn, Zr.

Ba, S, P, Ca and **Mg** were the most abundant elements in the studied wines, followed by **Cu**, **V**, **Pb** and **Na**.

Elements Ag, Au, Bi, Dy, Er, Eu, Ge, Ho, Lu, Ni, Pr, Sm, Tb, Ti, Tm, Yb were detected in a concentration lower than the LOQ.

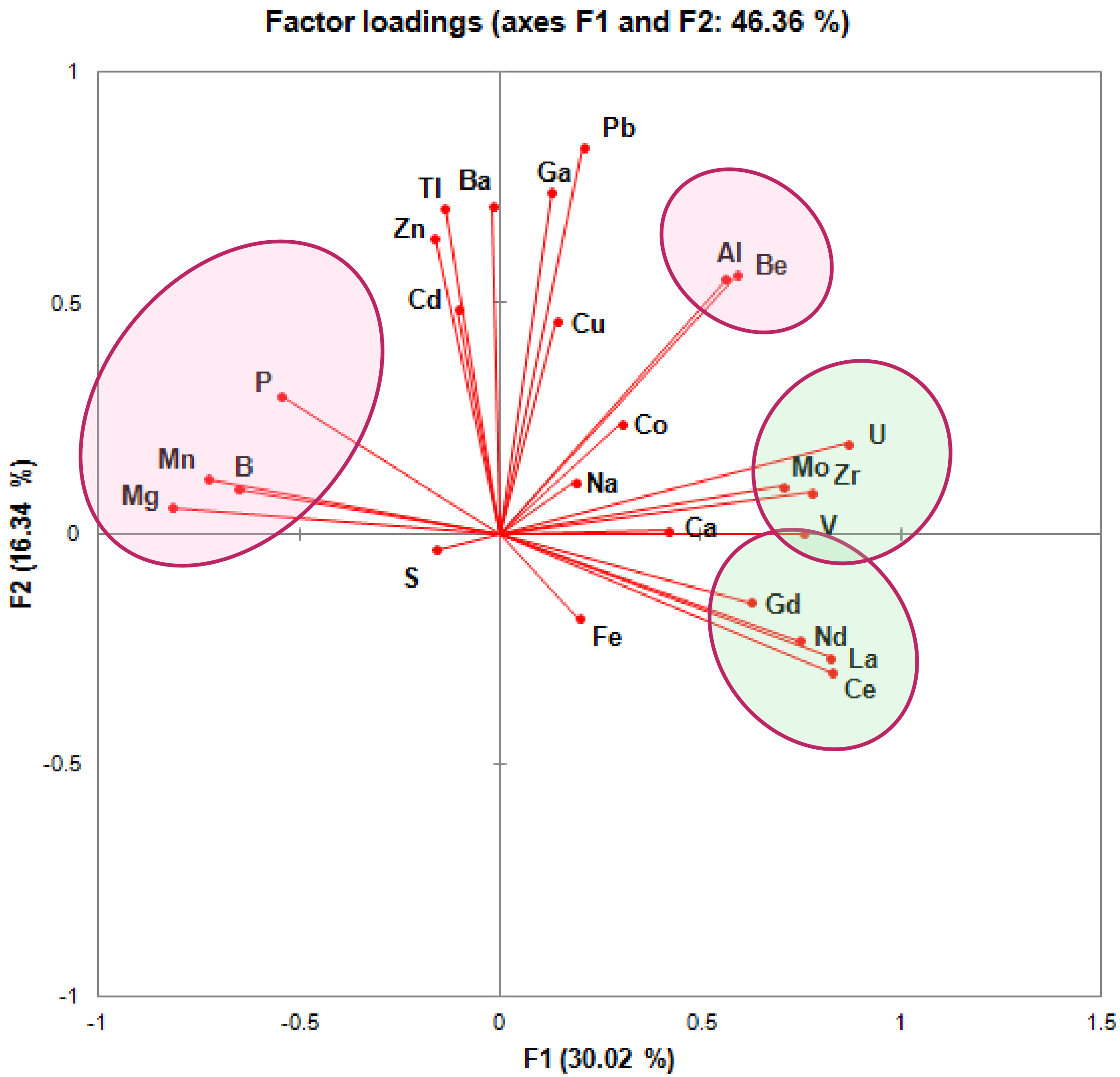
Descriptive statistics of the elements in wine

Statistic	*Min*	*Max*	*Md*	*X*	*Xg*	*V*	*SD*	*A*	*E*
Al (mg/L)	0.60	1.38	0.60	**0.67**	0.65	0.04	0.19	3.19	9.83
B (mg/L)	4.19	9.00	6.30	**6.49**	6.30	2.55	1.60	0.30	-1.43
Ba (µg/L)	0.00	324.00	136.00	**141.92**	46.03	5660.99	75.24	0.41	0.65
Be (µg/L)	0.00	9.30	0.50	**1.20**	0.31	5.22	2.29	3.12	9.03
Ca (mg/L)	48.80	89.00	71.00	**69.27**	68.07	166.17	12.89	-0.20	-1.21
Cd (µg/L)	0.00	1.19	0.21	**0.26**	0.11	0.08	0.29	2.36	5.69
Ce (µg/L)	0.00	3.70	0.25	**0.72**	0.26	0.68	0.83	2.28	6.29
Co (µg/L)	0.00	12.00	4.40	**5.13**	2.12	8.48	2.91	0.47	0.49
Cu (µg/L)	0.00	1027.00	46.00	**115.15**	22.31	44436.14	210.80	3.79	15.67
Fe (mg/L)	0.48	6.65	1.27	**1.89**	1.41	2.77	1.66	1.76	2.33
Ga (µg/L)	0.00	10.90	3.73	**4.30**	1.87	4.98	2.23	0.79	2.68
Gd (µg/L)	0.00	0.57	0.10	**0.12**	0.07	0.01	0.10	3.61	15.73
La (µg/L)	0.00	1.49	0.10	**0.28**	0.11	0.11	0.33	2.43	6.90
Mg (mg/L)	66.00	117.10	91.80	**89.79**	88.41	257.90	16.06	0.17	-1.18
Mn (mg/L)	0.72	2.01	1.25	**1.29**	1.24	0.14	0.37	0.41	-0.55
Mo (µg/L)	0.00	4.40	1.19	**1.62**	0.61	1.78	1.33	0.76	-0.66
Na (mg/L)	2.05	29.45	14.50	**13.49**	10.94	58.73	7.66	0.20	-1.02
Nd (µg/L)	0.00	2.10	0.20	**0.36**	0.16	0.18	0.42	3.25	12.65
P (mg/L)	63.30	288.00	143.70	**142.57**	130.92	3479.68	58.99	0.59	-0.01
Pb (µg/L)	0.00	79.00	10.10	**19.40**	5.42	454.34	21.32	1.66	1.99
S (mg/L)	91.00	391.00	145.00	**151.76**	144.28	3439.44	58.65	2.96	11.68
Tl (µg/L)	0.00	1.80	0.45	**0.54**	0.25	0.15	0.39	1.45	3.37
U (µg/L)	0.00	0.48	0.10	**0.14**	0.06	0.02	0.13	1.12	0.48
V (µg/L)	0.00	68.50	2.80	**11.75**	2.19	249.61	15.80	2.14	5.93
Zn (mg/L)	0.02	0.98	0.43	**0.43**	0.31	0.06	0.25	0.39	0.14
Zr (µg/L)	0.00	11.00	1.15	**3.07**	0.99	10.53	3.25	1.25	0.19

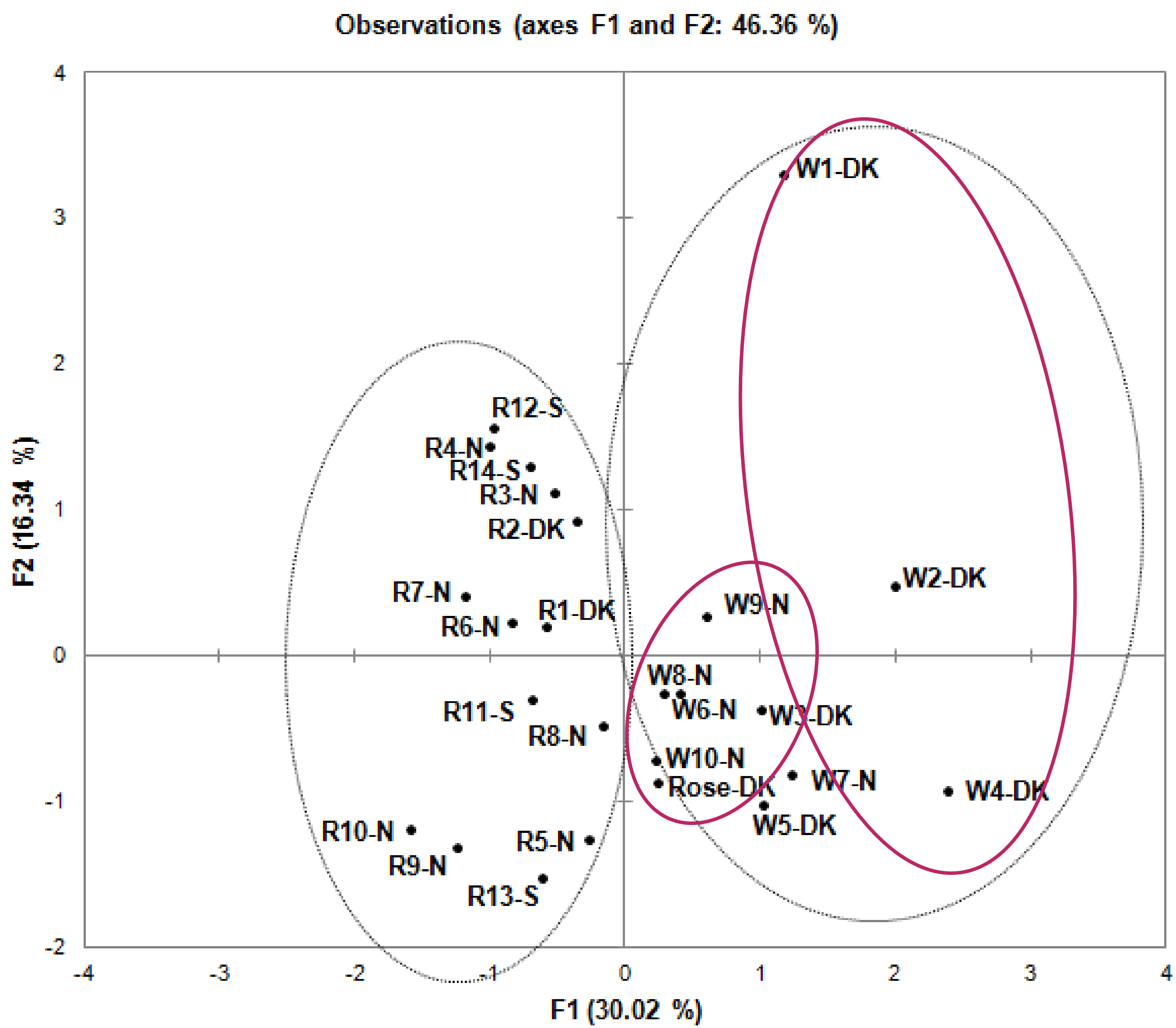
Principal component factor analysis

Matrix of dominant rotated factor loadings

	F1	*F2*	*F3*	*F4*	*F5*	*F6*
Al	0.563	0.552	-0.028	-0.078	**0.588**	0.002
B	**-0.650**	0.096	0.042	0.079	0.130	0.222
Ba	-0.019	**0.711**	-0.179	-0.570	-0.250	0.143
Be	**0.591**	0.563	-0.064	0.040	0.547	0.060
Ca	0.422	0.007	**-0.553**	-0.303	0.070	0.119
Cd	-0.104	0.486	0.274	**0.516**	-0.340	-0.145
Ce	**0.828**	-0.300	0.413	-0.144	-0.102	0.102
Co	0.302	0.239	-0.176	0.280	-0.458	**0.721**
Cu	0.142	0.461	0.059	-0.224	0.000	-0.234
Fe	0.198	-0.182	**-0.454**	0.398	-0.299	-0.077
Ga	0.130	**0.742**	-0.251	-0.505	-0.210	0.086
Gd	**0.623**	-0.148	0.603	-0.294	-0.236	0.050
La	**0.822**	-0.267	0.441	-0.140	-0.047	0.116
Mg	**-0.815**	0.058	0.310	-0.146	0.417	-0.022
Mn	**-0.725**	0.119	0.396	-0.021	-0.098	0.166
Mo	**0.704**	0.104	-0.463	0.407	-0.120	-0.013
Na	0.187	0.112	0.484	**0.578**	0.137	0.012
Nd	**0.745**	-0.231	0.535	-0.269	-0.091	0.081
P	-0.546	0.300	0.041	0.075	0.111	**0.714**
Pb	0.208	**0.836**	0.083	0.292	0.021	-0.296
S	-0.158	-0.035	0.055	0.062	**0.594**	0.234
Tl	-0.138	**0.705**	0.204	-0.107	-0.282	-0.191
U	**0.866**	0.195	0.174	0.063	0.130	0.244
V	**0.754**	0.001	-0.149	0.436	0.181	0.075
Zn	-0.161	**0.642**	0.475	0.280	-0.113	-0.032



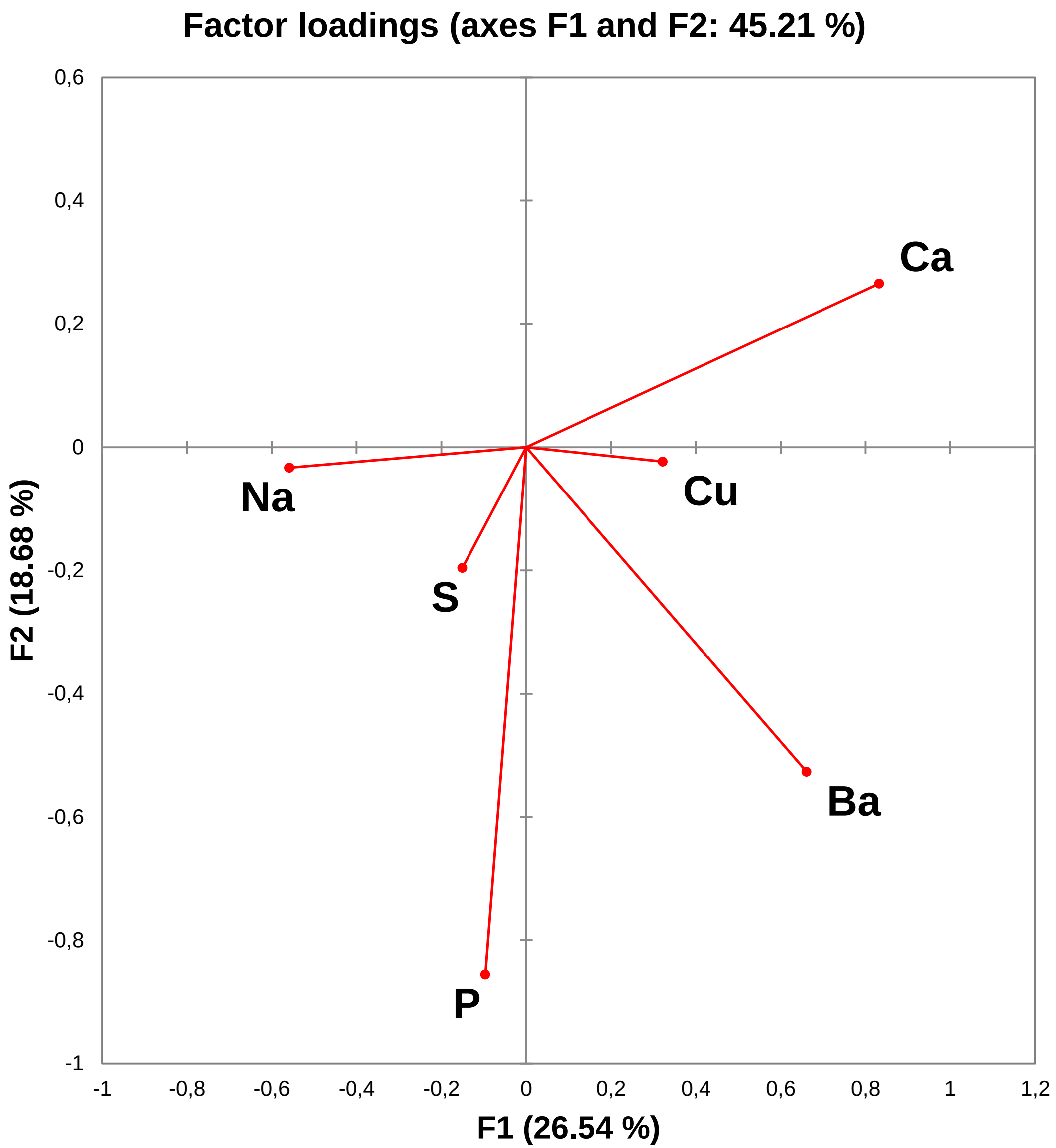
Factor loadings with F1 and F2 of the variables based on elements concentration in wines



- clear separation according to the **wine type** (**white vs. red**).

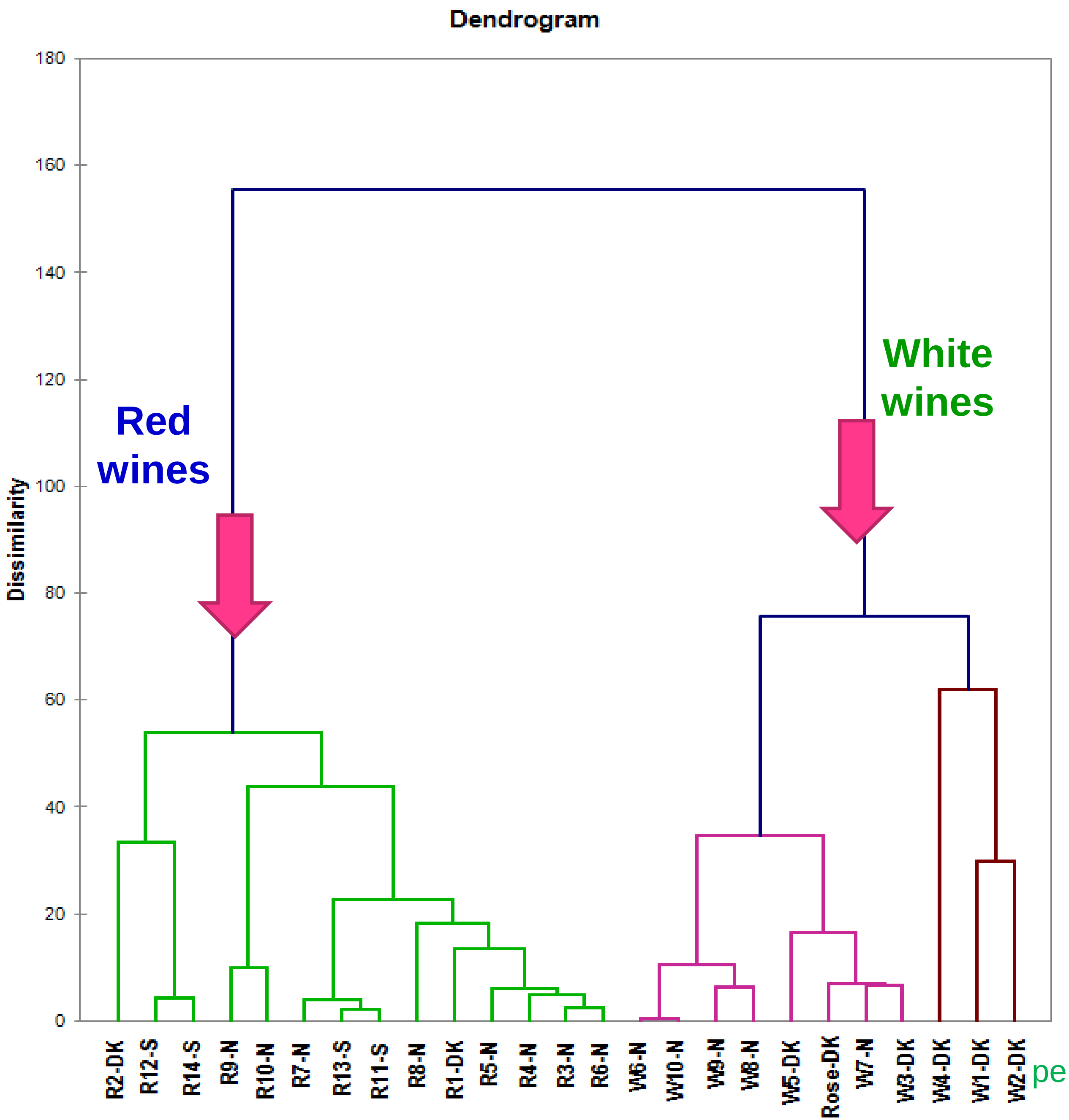
- grouping according to the **region**.
Negotino region
Demir Kapija region.

Observations with F1 and F2 of the variables based on elements concentration in wines and grouping of the wines according to wine type



Variables on discriminant elements concentration in wines

Cluster analysis



Wine grouping according to the wine type (red vs. white wines)

Dendogram obtained after the agglomerative Cluster Analysis performed on all elements quantified in wine samples

Ba and **P** - the dominant elements in red and white wines.

Ba

- ✓ naturally present in the soil as macroelement mainly - natural phenomena.
- ✓ its content strongly correlated to the nature of vineyard, rock weathering or chemical processes in soil.

P

- ✓ naturally present element, macroelement and essential for live.
- ✓ ranged from 63 to 288 mg/L, confirming the nutritional value of wines

S

- 91 to 206 mg/L in wines

since SO_2 is usually used in wine-making as an antioxidant and protective agent from enzymatic and non-enzymatic oxidation

Pb

- anthropogenic influence on the area where the vines are grown (especially if the vineyard is located near roads),
- contaminant during the wine-making process originating from the materials used for production of wine equipment.

Cu

- 21 to 1027 μg/L
- originate from agents used for vine protection (i.e. fungicides that contain Cu or $CuSO_4$)
- wine equipment produced from bronze and brass.

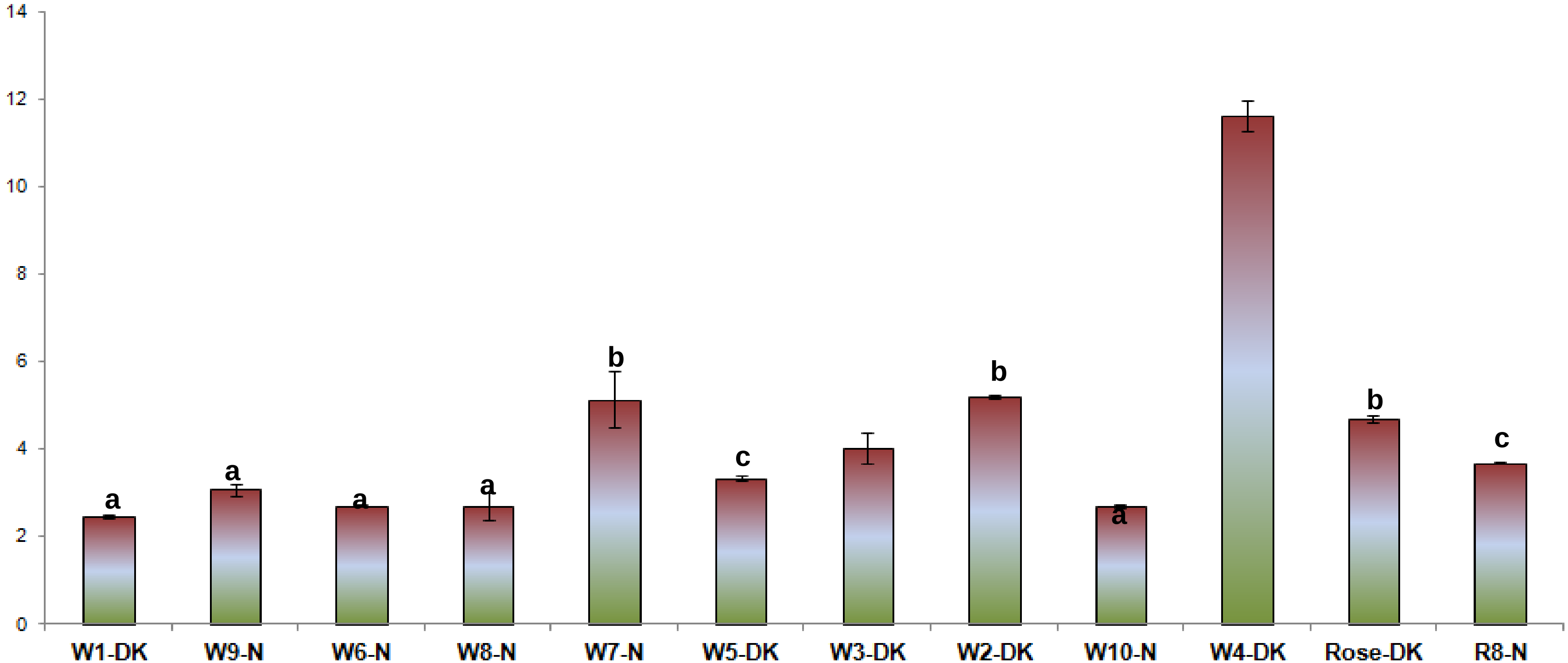
Heavy metals are toxic for the biological systems because of their capacity to deactivate the enzymes. Their maximal allowed content in food must be controlled.

Maximal allowed concentrations**: 1 mg/L - Cu** and **0.3 mg/L Pb**

The content of Cu and Pb in the Macedonian wines was lower than maximal allowed concentrations. **Bi** and **Cd** were **not detected**.

As a conclusion, studied Macedonian wines **did not contain** heavy hazard metals confirming their nutritional value with high level of macroelements such as **P, Na, Ba**.

Content of total rare earth elements in wines (μg/L)



Error bars represent standard deviation. Same superscripts at the bars indicate the values that are not significantly different ($p > 0.05$).

- **The concentration of rare earth elements (REE) was very low for most of these elements in the wines, ranged from 2.5 to 11.6 μg/L.**
- **The content of REEs is influenced mainly by application of bentonites for wine stabilization.**
- **White wines contained higher amount of REE than red ones, probably as a result of addition of agents for stabilization and finalization in a higher amount in white wines.**
- **In comparison to results reported by other authors the concentration of REEs in studied wines was lower.**

CONCULSION

- 25 Macedonian white, red and rose wines from three different wine regions, Demir Kapija, Negotino and Skopje, were discriminated according to the:
  - ✓ **wine type (white vs. red)** and
  - ✓ **geographical origin** applying factor and cluster analysis to the elements concentration.

- Inductively coupled plasma mass spectrometry (**ICP-MS**) methodology – determination of 42 elements (**Ag, Al, Au, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cu, Dy, Er, Eu, Fe, Ga, Gd, Ge, Ho, La, Lu, Mg, Mn, Mo, Na, Nd, Ni, P, Pb, Pr, S, Sm, Tb, Ti, Tl, Tm, U, V, Yb, Zn, Z**r).
- The main discriminant elements were **Ba, Ca, Cu, P, Na and S**.