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Supplementary information

Elemental composition as a tool for the assessment of type, seasonal variability, and geographical origin of wine and its contribution to daily elemental intake

Slađana Đurđić[a], Milica Pantelić[b], Jelena Trifković[a], Vesna Vukojević[a], Maja Natić[a], Živoslav Tešić[a] and Jelena Mutić[a,c]*

[a]University of Belgrade - Faculty of Chemistry, P.O. Box 51, 11158 Belgrade, Serbia

[b]Innovation Centre of Faculty of Chemistry Ltd, Studentski trg 12-16, 11000, Belgrade, Serbia

[c]Ghent University Global Campus, Incheon, South Korea

*Corresponding author (jmutic@chem.bg.ac.rs, tel/fax: +38113336745)

Content

Table S1. Region, vineyard, winery, wine sample and year of production

Region	Wine region	Winery	Wine sample	Year of production
Belgrade	Smederevo	Radmilovac	Burgundac crni A	2012
		Radmilovac	Burgundac crni B	2012
		Radmilovac	Burgundac sivi	2012
		Radmilovac	Burgundac	2013
		Radmilovac	Burgundac	2014
		Radmilovac	Cabernet Franc	2012
		Radmilovac	Cabernet Franc-standard	2013
		Radmilovac	Cabernet Franc-02*	2013
		Radmilovac	Cabernet Franc-010*	2013
		Radmilovac	Cabernet Franc-012*	2013
		Radmilovac	Cabernet Franc	2013
		Radmilovac	Cabernet Franc	2014
		Radmilovac	Cabernet Sauvignon	2012
		Radmilovac	Cabernet Sauvignon	2013
		Radmilovac	Cabernet Sauvignon	2014
		Radmilovac	Chardonnay[w]	2012
		Radmilovac	Chardonnay[w]	2013
		Radmilovac	Chardonnay[w]	2014
		Radmilovac	Merlot	2012
		Radmilovac	Merlot-standard	2013
		Radmilovac	Merlot-022*	2013
		Radmilovac	Merlot-025*	2013
		Radmilovac	Merlot-029*	2013
		Radmilovac	Merlot	2013
		Radmilovac	Merlot	2014
		Radmilovac	Petra[w]	2012
		Radmilovac	Prokupac	2012
		Radmilovac	Riesling Italijanski[w]	2012
		Radmilovac	Riesling Italijanski[w]	2013
		Radmilovac	Riesling Rajnski[w]	2012
		Radmilovac	Riesling Rajnski[w]	2013
		Radmilovac	Riesling Rajnski[w]	2014
		Radmilovac	Sangiovese	2012
		Radmilovac	Sauvignon Blanc[w]	2012
		Radmilovac	Sauvignon Blanc[w]	2013
		Radmilovac	Sauvignon Blanc[w]	2014
		Radmilovac	Smederevka[w]	2014
		Radmilovac	Shiraz	2012
Central	Topola	Radovanović	Cabernet Sauvignon	2010
	Topola	Radovanović	Cabernet Sauvignon	2011

Serbia	Negotin	Dajić	Cabernet Sauvignon	2009
	Negotin	Tanica pimnice	Cabernet Sauvignon	2011
	Negotin	Dajić	Game	2009
	Župa	Rubin	Merlot-Tarra Lazarica	2009
	Župa	Vino Budimir	Prokupac-Triada	2006
	Župa	Vino Budimir	Tamjanika	2014
	Župa	Radmilovac	Plovdina	2014
	Knjaževac	Jović	Vranac Potkranjski	2009
Vojvodina	Palić	Čoka	Cabernet Sauvignon-Lederer	2010
	Palić	Čoka	Cabernet Sauvignon	2011
	Palić	Čoka	Merlot-Lederer	2010
	Palić	Čoka	Merlot	2011
	Vršac	Radmilovac	Merlot	2014
	Fruška gora	Radmilovac	Prokupac sremski	2014
South Serbia	Prokuplje	Stari dani	Cabernet Sauvignon	2009
	Prokuplje	Stari dani	Cabernet Sauvignon	2014
	Prokuplje	Petrović	Carsko crveno	2011
	Prokuplje	Petrović	Cabernet Sauvignon	2012
	Prokuplje	Petrović	Cabernet Sauvignon	2011
	Prokuplje	Petrović	Prokupac	2011
	Prokuplje	Radmilovac	Crna Tamjanika	2014
	Prokuplje	Stari dani	Prokupac	2014
	Prokuplje	Stari dani	Vranac	2014

[w] White wines, all other are red wines

* Clones: Merlot namely No 022, 025 and 029 and Cabernet Franc No 02, 010 and 012

Table S2. Instrument operating conditions for ICP-OES and ICP-Q-MS

ICP- OES	
Nebulizer	Concentric
Spray chamber	Cyclonic
Rf power (W)	1150
Principal argon flow rate (L/min)	12
Auxiliary argon flow rate (L/min)	0.5
Nebulizer argon flow rate (L/min)	0.5
Sample flow rate (mL/min)	1.0
Selected wavelengths (nm)	Fe (259.9); Na (589.5); Ca (373.6); Mg (279.5); K (766.4); Rb (780.0)
Detection limits (µg/L)	Fe (0.2); Na (0.2); Ca (0.3); Mg (0.2); K (0.4); Rb (0.1)
ICP- OES (hydride generation)	
Reductor	0.1% $NaBH_4$ in 0.5% NaOH
Acid	8.0 mol/dm^3 HCl
Carrier flow rate (L/min)	0.4
Rf power (W)	1150
Wavelengths (nm) of As	189.0
Detection limits (µg/L)	0.05
ICP-Q-MS	
Rf power (W)	1548
Gas flows (L/min)	13.9;1.09;0.8
Acquisition time	3 x 50s
Points per peak	3
Dwell time (ns)	10
Detector mode	Pulse
Measured isotopes (normal mode)	^{9}Be, ^{27}Al, ^{51}V, ^{59}Co, ^{60}Ni, ^{66}Zn, ^{111}Cd, ^{121}Sb, ^{137}Ba, ^{208}Pb
Measured isotopes (collision cell mode)	^{52}Cr, ^{55}Mn, ^{78}Se
Detection limits (µg/L)	Be (0.1), Al (2.0),V (0.02), Co (0.02), Ni (0.3), Zn (0.4), Cd (0.05), Sb (0.08), Ba (0.02), Pb (0.1), Cr (0.3), Mn (0.4), Se (0.2)

Table S3. Concentration of major and trace metals in wines from different viticulture countries

	Czech[30]	Croatia[16]	Romania[33]	Argentina[31]	Spain[15]	Turkey[36]	Belgium[32]	Spain[27]	Macedonia[5]	this study
K (mg/L)	493–3056				470–1014			423-1375		298-1167
Mg (mg/L)	48.9–108				56.7–93.4		9.7--14.0	71.2-153.3	66-117.1	38-124.8
Ca (mg/L)	47.7–210			10-15	44.7–104		4.1-10.3	48.8-161.0	48.8-89.0	41.2-131.2
Na (mg/L)	2–62				9.55–59.1			12.33-191.5		2.94-37
Fe (mg/L)	0.929–5.2	2.145-7.526		0.480–0.790	0.72–7.16	0.32-5.79		0.55-7.56	0.48-6.65	0.01-2.8
Rb (mg/L)	0.096–2.470		0.22-2.066				0.176-0.630			0.79-4.7
Mn (µg/L)	282–3260	501-1729	223-3078		140–1140	121.4-1822	56-228	640-4000	715-2011	294-3310
Al (µg/L)	132–1665	644-2431		17.0–18.0	630–3120		19.1-64.0		0.60-1.38	514-2189
Zn (µg/L)	33.9–1172	156-1153	57-1443	24–130	80–1180	156.6-5242	23-84	110-1070	20-980	215-2585
Cu (µg/L)	12.8–6827	62.7-726	26-2595	23–28		29.2-525	1.24-21.1		0-1027	24-1684
V (µg/L)	0.015–70.2	1.92-17.8	18.6-238.0		20–820		0.03-1.4	0.32-193	0 -68.5	0.02-14.6
Ba (µg/L)	41.6–193	28.2-162.3			10–80		4.8-48.3	96-263.8	0 -324	20.6-301.2
Pb (µg/L)	10.9–1253	9.97-71.8	17.0-235.9	50–90		ND-25.92		4.64-60.32	0-79.0	9.3-188.2
Ni (µg/L)	19.8–34.5	15.3-41.9	1.4-322.7	ND		45.29-3605.65	0.42-1.40	18.85-73.24		8.5-420.5
Cr (µg/L)	27–88.3	6.5-29.9	60.96-1725.8	ND–7.0		7.023-175.01				0.1-20.7
Sb (µg/L)	0.18–29.7	0.253-1.79						210-930		0.06-18.65
As (µg/L)	1.66–15.2	0.69-9.66								1.2-37.9
Co (µg/L)	0.359–5.24	1.74-5.96	0.3-42.1			2.30-16.53			0 - 12.0	0.4-9.6
Be (µg/L)	0.05–3.02	0.213-2.393	6.7-8.05						0-9.3	0-7.01
Cd (µg/L)	0.055–3.37	0.200-1.88		1.0–4.7		ND-9.53		0.21-2.65	0 -1.19	0.07-11.1
Se (µg/L)		0.653-3.10								0.06-10.52

Table S4. Pearson's correlation coefficients (*r*) between elements in white wines

	As	Ba	Be	Cd	Co	Cr	Ni	Pb	Sb	Se	V	Al	Mn	Zn	Cu	Ca	Fe	K	Mg	Na	Rb
As	1.000																				
Ba	-0.671	1.000																			
Be	-0.110	0.230	1.000																		
Cd	0.113	-0.427	-0.040	1.000																	
Co	0.271	-0.359	-0.221	-0.266	1.000																
Cr	0.409	-0.290	-0.093	0.332	0.074	1.000															
Ni	-0.052	-0.350	0.180	0.417	-0.199	0.294	1.000														
Pb	0.444	-0.414	0.140	**0.607**	-0.286	0.335	0.313	1.000													
Sb	-0.100	-0.005	0.209	-0.201	0.047	0.218	0.309	-0.043	1.000												
Se	-0.009	0.114	0.021	-0.066	-0.090	0.076	0.018	0.268	-0.092	1.000											
V	-0.315	**0.620**	0.288	-0.055	-0.394	0.082	-0.215	-0.233	-0.308	-0.181	1.000										
Al	-0.013	0.162	**0.633**	0.288	**-0.619**	-0.214	-0.043	0.144	-0.219	-0.109	0.422	1.000									
Mn	0.251	-0.184	-0.256	0.233	-0.258	0.237	-0.359	0.150	0.185	-0.126	-0.072	0.221	1.000								
Zn	0.377	-0.293	0.075	0.414	-0.221	0.326	0.207	**0.918**	-0.079	0.292	-0.105	0.000	0.084	1.000							
Cu	0.300	-0.344	0.007	0.392	-0.268	0.198	0.338	**0.882**	-0.050	0.460	-0.297	-0.057	0.041	**0.925**	1.000						
Ca	0.299	-0.340	-0.127	0.463	**-0.607**	0.148	0.054	0.522	-0.003	0.033	-0.126	0.394	**0.740**	0.382	0.447	1.000					
Fe	0.002	-0.005	-0.131	0.406	-0.479	0.053	-0.174	0.199	0.038	-0.326	0.349	0.365	**0.687**	0.169	0.081	**0.639**	1.000				
K	-0.040	0.476	0.288	-0.369	-0.082	-0.111	-0.293	-0.033	0.137	0.392	0.195	0.118	-0.025	0.092	0.094	-0.258	-0.021	1.000			
Mg	0.247	-0.444	-0.473	0.140	-0.052	0.463	0.136	0.266	0.274	-0.153	-0.243	-0.374	0.470	0.283	0.258	0.508	0.348	-0.438	1.000		
Na	**-0.647**	**0.562**	0.239	0.043	-0.341	-0.024	0.321	-0.187	0.055	-0.314	**0.610**	0.075	-0.471	-0.123	-0.228	-0.336	0.053	-0.132	-0.136	1.000	
Rb	-0.253	0.107	-0.370	0.027	0.159	0.176	0.092	-0.020	0.139	0.196	-0.037	-0.550	-0.201	-0.048	-0.035	-0.218	0.024	-0.081	0.365	0.268	1.000

Correlation is significant at 99% confidence level ($r_{critical}$ = 0.560, n = 17)

Table S5. Pearson's correlation coefficients (*r*) between elements in red wines

	As	Ba	Be	Cd	Co	Cr	Ni	Pb	Sb	Se	V	Al	Mn	Zn	Cu	Ca	Fe	K	Mg	Na	Rb
As	1.000																				
Ba	**-0.469**	1.000																			
Be	-0.191	**0.622**	1.000																		
Cd	0.091	-0.014	0.073	1.000																	
Co	-0.002	0.181	0.195	0.175	1.000																
Cr	**-0.578**	**0.546**	**0.568**	0.074	0.104	1.000															
Ni	**-0.429**	**0.705**	**0.503**	-0.002	0.196	**0.421**	1.000														
Pb	-0.030	0.022	0.104	**0.753**	0.339	0.092	0.135	1.000													
Sb	-0.116	0.053	0.015	-0.019	0.239	0.171	0.110	0.042	1.000												
Se	**0.430**	-0.237	-0.242	0.026	0.028	**-0.412**	-0.149	-0.104	-0.202	1.000											
V	-0.131	0.308	0.641	0.004	0.090	**0.452**	0.070	0.098	-0.057	-0.156	1.000										
Al	-0.240	0.327	**0.531**	-0.072	0.082	**0.503**	0.258	-0.021	0.187	-0.192	0.425	1.000									
Mn	**-0.441**	**0.752**	**0.443**	0.021	0.246	**0.475**	**0.511**	0.056	-0.019	**-0.377**	0.334	0.261	1.000								
Zn	-0.052	0.072	0.085	-0.178	0.047	0.140	0.225	0.193	0.238	-0.053	-0.032	0.259	-0.123	1.000							
Cu	-0.127	0.024	0.020	-0.011	0.223	0.046	0.282	**0.546**	0.210	-0.065	0.017	0.134	-0.060	**0.624**	1.000						
Ca	**0.444**	-0.076	-0.008	0.121	0.071	-0.322	-0.171	0.095	-0.051	0.347	0.024	0.047	-0.119	0.299	0.090	1.000					
Fe	0.170	-0.252	0.046	0.098	-0.183	-0.022	-0.234	0.035	0.054	-0.052	0.219	0.084	-0.060	0.213	-0.026	0.254	1.000				
K	-0.273	0.205	0.125	-0.044	-0.119	0.063	0.144	-0.191	-0.202	0.254	0.055	-0.009	0.096	-0.337	-0.268	-0.007	-0.247	1.000			
Mg	0.135	-0.038	0.041	0.117	0.073	0.042	-0.011	0.160	0.258	-0.228	0.012	0.332	0.193	**0.463**	0.179	0.314	0.326	**-0.496**	1.000		
Na	**-0.399**	**0.520**	0.360	0.008	0.035	**0.440**	0.289	0.077	-0.057	-0.292	**0.412**	0.375	**0.700**	-0.011	-0.005	-0.190	0.141	0.035	0.189	1.000	
Rb	-0.087	-0.080	-0.034	0.253	0.140	0.048	-0.027	0.109	0.100	0.124	-0.162	0.027	-0.125	-0.063	-0.161	0.041	-0.156	0.251	0.144	-0.222	1.000

Correlation is significant at 99% confidence level ($r_{critical}$ = 0.376, n = 46)

Table S6. Statistical parameters of PCA models

		PC1	PC2	PC3	PC4	PC5	PC6	PC7
Wine type	Eigenvalues	5.14	3.20	2.32	1.64	1.38	1.21	1.09
	Variance (%)	24.48	15.24	11.07	7.79	6.56	5.76	5.19
Seasonal variability	Eigenvalues	4.57	3.20	2.70	2.14	1.60	1.29	1.10
	Variance (%)	21.77	15.21	12.86	10.19	7.60	6.14	5.22
Regional origin	Eigenvalues	5.39	3.01	2.37	2.05	1.96	1.50	1.15
	Variance (%)	25.68	14.33	11.27	9.75	9.31	7.17	5.42