Vitis **51** (3), 111–118 (2012)

Geochemical influence of soil on leaf and grape (*Vitis vinifera* L. 'Cencibel') composition in La Mancha region (Spain)

J. A. Amorós Ortiz-Villajos[1), 2)], F. J. García Navarro[1), 2)], C. Pérez de los Reyes[1), 2)], J. A. Campos Gallego[1)], S. Bravo Martín-Consuegra[1), 2)], R. Jiménez Ballesta[2), 3)] and R. García Moreno[4)]

[1)] Escuela de Ingenieros Agrónomos, Universidad de Castilla La Mancha, Ciudad Real, Spain
[(2)] Instituto de Geología Aplicada, Universidad de Castilla La Mancha, Ciudad Real, Spain
[(3)] Departamento de Geología y Geoquímica, Facultad de Ciencias, Universidad Autónoma de Madrid, Madrid, Spain
[(4)] Departamento de Ciencias da Navegación e da Terra, Facultad de Ciencias, Universidade da Coruña, Coruña, Spain

Summary

The main purpose of the study was to evaluate major and trace elements contained in topsoil from representative plots of vineyards located in La Mancha, Spain, to obtain an elemental fingerprint of vines.

The samples evaluated were obtained from topsoil in six different plots, belonging to the region of La Mancha, characterized by the cultivation of vineyards (near 189.127 ha). Twenty different vines from each plot were chosen to take samples from grapes, petioles and leaves. Analyses were carried out by X-ray Fluorescence applied on soils and dried vegetal matter. Biological Absorption Coefficient (BAC) was calculated to assess the uptake of minerals by vines as a function of their specific content in soil.

The BAC in leaves and grapes was very similar for all studied elements. High contents of Ca, Sr, Ni and rare earth elements (La, Ce and Nd) were found along with low contents in Al, Zr, Ba, Cu, Zn and Pb, and normal contents in the rest of the elements.

BAC in grapes was lower for the majority of the studied elements but it is interesting to underline the contents of Cs, K, Nb, Ce, Zn and Sr as possible markers of soil fingerprinting in the resulting wines.

K e y w o r d s : Trace elements, Strontium, vine physiology.

Introduction

The chemical interaction between soil-plant systems is characterized by the contents of the different elements. In this sense, each particular system has its own specific constituents. The elemental composition in wines and grapes has been extensively studied in order to evaluate the characteristics associated with the different regions and varieties, mainly in an attempt to obtain an elemental fingerprint for products to certify designations of origin. In general, the vineyards cultivated in the region of La Mancha produce wines with their own designation of origin (D.O. La Mancha). This region represents the world's largest vineyard area, with 189,127 ha, and it is formed by four provinces, Toledo, Albacete, Cuenca and Ciudad Real (Hidalgo 1980). Evaluation of the geochemical properties of the vines and comparison of the elemental contents in soils could be of great interest for the region. For example, it would be possible to assess the influence of other factors on the composition of wines along with the soil plant interactions in major and trace elements, and to detect any external variation in the elemental contents, mainly as a consequence of diffuse pollution. The soils in the aforementioned area originate from Tertiary sediments (Miocene) (Hidalgo 1980). These soils were formed over Ordovician-Silurian rocks and originate from the erosion and weathering of the old Hercinic socket. In general, the soils of the region are classified as Luvisols, with rhodic or chromic character, due to the presence of iron oxides (FAO ISRIC ISSS, 2006). The main materials found over the Hercinic socket result from the weathering and erosion of quartzite and materials from the schist-greywacke complex. However, the soils from the region of Ciudad Real have not been studied in great detail.

The different properties of wine cultivars are greatly influenced by soil characteristics, chiefly texture and content of macro and micronutrients. Several studies have been carried out on Mediterranean regions and areas of influence to investigate soil origins, parent materials and their characteristics (Carlevalis *et al.* 1992, Atalay 1997, García and Santos 1997, Yaalon 1997, Yassoglou *et al.* 1997, Ortiz *et al.* 2002, Bronger and Sedov 2003). Indeed, recently published studies have focussed on the area under consideration in this paper (De la Horra *et al.* 2008, Conde *et al.* 2009).

The study of geochemical soil composition provides information, along with other complementary data, about fertility and the availability of nutrients for plants. Major elements provide information about total structural components and potential nutrients (Wild 1992, Lanyon *et al.* 2004, White 2009), while contents of trace elements give an insight into the geochemical origin (García *et al.* 2009) and potential toxicities (Conde *et al.* 2009) of the soil.

The metabolism of trace elements in plants has been widely studied (Wild 1992, Kabata-Pendias 2001). However, every plant-soil system (Kabata-Pendias 2001, Molina *et al.* 2006) has to be specifically studied, since the behaviour could differ depending on the elements present in a particular system. In all cases studied previously, plant composition (leafs, fruits, juices, tubers, etc.) always reflected the chemical properties from the environment of

Correspondence to: Dr. R. García Moreno, Departamento de Ciencias da Navegación e da Terra, Facultad de Ciencias, Universidade da Coruña, A Coruña, Spain. E-mail: chgarcia@telefonica.net; rosario.garciam@udc.es

cultivation (Kabata-Pendias 2001, Casañas *et al.* 2003, Di Giacomo *et al.* 2007, Chopin *et al.* 2008, Pessanha *et al.* 2010). In the particular case of grape composition, the elemental content will be influenced by soil composition as well as the variety and maturity of the cultivars and the climatic conditions (Pohl 2007).

The first attempt to evaluate the provenance of a wine by studying multi-elemental analysis was reported by Kwan *et al.* (1979). More recently, several studies have been carried out in different areas and, as pointed out by Separinas *et al.* (2008), the use of Inductively Coupled Plasma has provided a wider range of elements and much lower limits of detection. The metal content found in cultivars was independent of the age of vines and was more related to the metal content in the soil at the time of analysis. In this sense, the multi-elemental analysis of grapes became very important for the producer to demonstrate the authenticity of the area of provenance and to show potential situations of specific metal contamination in soils (Galani-Nikolakaki *et al.* 2002, Kment *et al.* 2005, Galgano *et al.* 2008, Paneque *et al.* 2009, Fiket *et al.* 2011). Factors that have become very important include the variability of elements in soils, the behaviour of plants with a specific element, the amount of a specific detectable trace element, the geographic location and the global environment and its interactions. All of these properties can define the chemical composition of a particular grape, and subsequently that of the wine, thus emphasizing the importance of knowledge of the “terroir” for each particular wine (Hugget 2006). In the case of Spanish wines, most products with a designation of origin have been studied in relation to their soils of provenance (Barbaste *et al.* 2002, Gonzálvez *et al.* 2009, Paneque *et al.* 2010), except for the various vineyards of La Mancha, where the vines have poorly been studied in relation to the soil properties, particularly in terms of their contents of trace and major elements (Amorós *et al.* 2008, Amorós *et al.* 2010).

Given the importance of the aspects outlined above, the main objective of the work described here was to characterize the contents of major and trace elements in different parts of the vines from the region of Campo de Calatrava, the varied soils and vineyards of which are representative of La Mancha Region (Ciudad Real, Spain). Another aim was to assess the pattern in the accumulation of major and trace elements in the different parts of the vines.

Materials and Methods

S t u d i e d a r e a : The area under investigation was near to the municipality of Carrión de Calatrava in the province of Ciudad Real (Fig. 1). This location was chosen because of its soil diversity and because the vineyards cultivated are of the 'Cencibel' variety ('Tempranillo') grafted onto '110-Richter'. Dry farming and low vine conduction, pruned in spurs is the traditional management regime in this area (the La Mancha Region has its own designation of origin, D.O. La Mancha). These soils represent 27.2 % of the total regional area dedicated to the cultivation of the wine grape (Hidalgo 1980, Amorós *et al.* 2008). The main use of the cultivars is in the production of premium-quality wines (Pillet 2007).

The area is formed by a smooth topography with alternating quartzitic hills (Amorós *et al.* 2010) and Miocene plains. The valleys show hydromorphic soils and quaternary sediments. In addition, some volcanic intrusions could be present within the described elements. The great variability of soils with different geological origins and specific evolutions offers one of the greatest edaphically diverse regions of the World (De la Horra *et al.* 2008, Carlevalis *et al.* 1992).

The altitude and locations of the plots are indicated in Tab. 1. The samples evaluated were obtained from topsoil in six different plots, with three samples taken from

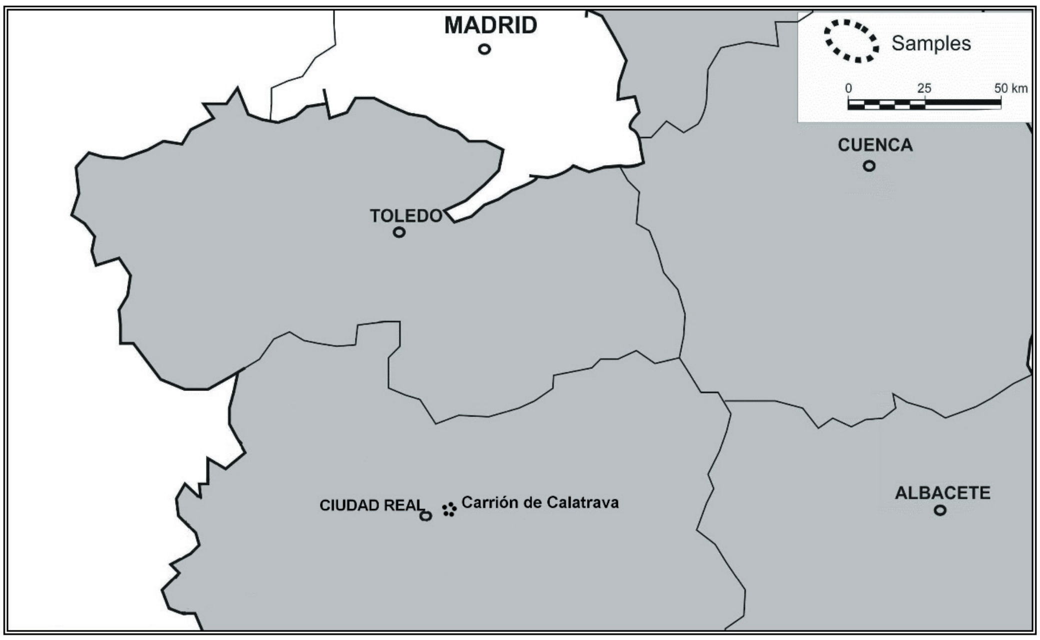

Fig. 1: Location of plots.

Table 1

Properties of plots. Altitude, location, organic matter, active lime and total carbonates

Plot identification	Altitude (m)	Coordinates	Organic matter (%)	Active lime (%)	% $CaCO_3$
M1	623	39º05'09.1" – 03º51'09.1"	1.9	2.50	4.5
M2	627	39º03'31.9" – 03º49'00.6"	1.5	7.38	16.4
M3	636	39º02'41.1" – 03º52'12.3"	1.2	10.63	9.8
M4	621	39º03'23.3" – 03º52'31.9"	3.2	10.63	23.9
M5	618	39º03'11.7" – 03º52'36.2"	1.0	3.00	3.0
M6	631	39º02'08.7" – 03º52'33.0"	3.6	14.88	25.5

each plot. At the same locations, a total of 20 different vines from each plot were chosen to take samples from grapes, petioles and leaves. The samples were kept in bags, marked, dated and submitted to the same elemental analysis procedure.

Analytical Procedures: All analytical determinations were carried out according to SCS-USDA guidelines (SCS-USDA 1972). All samples were extracted and analysed in triplicate.

Soil texture was determined using the hydrometer method (Gee and Bauder 1986). Soil pH was measured in H_2O and in 0.1 M KCl using a 1:2.5 soil/solution ratio. Electrical conductivity was measured on a 1:5 soil: water extract. The soil organic matter was quantified by the Walkley and Black wet oxidation method (Nelson and Sommers 1982). Soil colour was measured using Munsell Color Charts (Munsell Color Co. 1998). The determination of calcium carbonate was carried out with a calcimeter. The active calcium carbonate equivalent or 'active lime' was determined with NH_4-oxalate as described by Drouineau (1942).

The trace elements analysis with the major and trace elements obtained as percentage (%) and ppm (mg·kg^{-1}), respectively.

Soils samples were taken at the beginning of the summer of 2010. On 16th July 2010, 20 leaves were taken from 20 vines from each plot. The leaves were taken from opposite the first cluster in order to ensure that all the leaves were of the same age. The leaves were dried and the limbo and petiole were separated. About 2 g of each sample were hand milled and analysed using the same fluorescence spectrometer.

On 28th August 2010, 500 grains of grapes were taken from each plot. The grapes were dried, lyophilised and hand milled prior to analysis using the same fluorescence spectrophotometer. All of the vegetal material was analysed after fine milling in a Teflon mill.

The software packages Microsoft Office EXCEL 2007 (Copyright© Microsoft 2008) and STATGRAPHICS Plus 5.1 (Copyright© 1994-2000 Statistical Graphics Corp.) were used for statistical analyses and to produce figures.

Results and Discussion

Soil characteristics: General data for the soils of the studied plots are given in Tabs 1 and 2. Even soils located in plots next to each other show large variation in their properties. In particular, the organic matter content is highly variable due to the different manure systems used by each farmer. These soils have a basic pH and they contain medium to high contents of calcium carbonate. These soil characteristics are very common in the region of La Mancha (Carlevalis *et al.* 1992, Hidalgo 1980, De la Horra *et al.* 2008). In this particular case, the mobilization of metallic elements that are normally adsorbed in clay (Kabata-Pendias 2001) is more effective in acidic media (Wild 1992, White 2009). The electrical conductivity results do not suggest any problem related to salinity (Wild 1992). The most frequent textural class is the loam type, with a clay content that does not exceed 20 %.

Soils were classified as Chromic Luvisols or Petric Calcisols (FAO ISRIC ISSS, 2006). A description of the soils has been published previously (De la Horra *et al.* 2008, Carlevalis *et al.* 1992, Amorós *et al.* 2010).

Contents of major elements in the soil-vine system: The results for the total contents of major and trace elements are shown in Tab. 3 for each plot. The data are arranged from 1 to 6, according to the number of plot. The first six results are denoted CE and these represent the soils. The CE designation comes from the name of the vine variety cultivated in the studied plots, which is known as 'Cencibel' in La Mancha ('Tempranillo' is the best-known name worldwide since it is used in La

Table 2

Properties of plots. Texture, pH, electric conductivity and colour

Plot identification	pH (1:2.5)	Texture	E. C. (dS/m)	Colour Dry
M1	8.31	Sandy loam	0.77	5 YR 4/6 (yellowish red)
M2	8.43	loam	0.77	7.5 YR 5/4 (brown)
M3	8.11	loam	0.73	5 YR 3/4 (reddish brown)
M4	8.18	loam	0.83	7.5 YR 4/3 (brown)
M5	8.44	Sandy loam	0.78	7.5 YR 3/2 (dark brown)
M6	8.11	loam	0.85	7.5 YR 4/4 (brown)

Table 3

Major and trace elements in soils, leaves and fruits. The identification starts with the number of the plot, from 1 to 6, to show which sample belongs to each plot. CE is the identification for the soil samples, CEH for the leave samples, CEP for petiole samples and CEU for grape samples. The concentrations are expressed in % for major elements (from Na to K) and in ppm for trace elements (from V to Nd). All results are given on the basis of dry matter

	Na	Mg	Al	Si	P	S	Ca	Mn	Fe	K	V	Cr	Co	Ni	Zn	Rb	Sr	Nb	Cs	Ba	Ce	Pb	Nd
1CE	0.106	0.844	7.959	24.457	0.072	0.045	7.672	0.059	0.547	3.722	64.40	61.80	10.60	29.40	45.00	73.70	78.50	14.30	7.00	313.50	70.20	22.80	35.10
2CE	0.118	0.940	3.368	25.237	0.086	0.068	8.729	0.055	0.580	3.061	53.40	47.00	10.60	25.80	45.50	70.10	239.00	13.40	3.50	312.00	60.30	24.60	25.70
3CE	0.070	0.687	4.363	26.403	0.094	0.034	4.540	0.057	0.844	5.398	110.90	97.40	13.70	58.80	47.00	52.90	78.80	24.20	4.70	317.50	87.20	18.10	40.30
4CE	0.042	0.926	2.481	19.151	0.082	0.048	15.171	0.114	0.674	4.147	90.50	93.90	15.20	69.70	44.90	42.20	314.70	23.70	0.00	283.70	52.50	17.40	21.90
5CE	0.090	1.069	2.707	31.202	0.079	0.045	4.792	0.046	1.788	3.140	67.60	65.80	10.00	33.50	29.10	44.40	264.90	15.90	1.00	242.80	59.00	15.30	24.80
6CE	0.064	1.060	2.666	16.867	0.104	0.050	18.131	0.057	0.541	3.566	55.30	58.60	11.80	40.40	40.00	53.30	165.40	15.80	0.00	254.80	53.60	19.80	26.70
1CEH	0.004	0.329	0.060	0.677	0.123	0.262	2.490	0.007	0.605	0.046	6.20	5.20	2.80	1.50	14.10	3.70	47.60	4.40	3.50	33.00	10.30	3.80	7.40
2CEH	0.004	0.419	0.050	0.608	0.136	0.177	2.652	0.005	0.354	0.047	4.90	5.00	2.40	1.60	14.10	3.20	117.00	3.20	6.40	33.60	14.30	4.30	6.70
3CEH	0.004	0.358	0.075	1.242	0.208	0.219	2.823	0.010	0.884	0.077	8.90	5.50	2.80	2.50	15.90	4.10	114.70	4.50	4.80	42.80	16.80	4.70	6.10
4CEH	0.011	0.490	0.052	1.085	0.181	0.211	3.768	0.012	0.576	0.065	8.00	5.70	3.10	2.00	13.90	3.20	181.70	4.30	3.00	39.70	6.20	4.30	1.20
5CEH	0.018	0.615	0.047	0.580	0.220	0.210	1.837	0.008	0.712	0.050	8.50	5.00	3.40	2.40	13.30	5.20	135.30	4.60	6.20	41.90	11.10	0.00	3.60
6CEH	0.004	0.441	0.048	0.728	0.208	0.250	2.931	0.019	1.271	0.048	5.10	4.70	2.20	2.30	22.40	4.10	105.00	4.50	3.00	45.90	5.90	4.20	0.80
1CEP	0.080	0.616	0.010	0.041	0.094	0.092	1.552	0.004	1.223	0.005	4.80	4.40	3.00	0.90	24.10	6.30	55.90	4.30	2.80	32.90	9.70	0.80	5.90
2CEP	0.029	0.045	0.007	0.027	0.072	0.057	1.473	0.005	0.729	0.002	5.40	4.50	2.50	1.00	15.30	3.30	108.60	3.10	3.90	37.70	6.50	3.00	3.30
3CEP	0.004	0.742	0.007	0.009	0.133	0.080	2.159	0.005	1.135	0.002	4.20	4.30	2.90	0.80	11.90	4.60	108.10	4.20	3.20	45.20	12.20	3.70	4.80
4CEP	0.010	0.683	0.006	0.027	0.135	0.093	2.160	0.007	0.657	0.002	4.20	4.40	2.60	0.80	22.50	4.10	152.90	4.40	9.90	46.20	13.00	3.20	7.70
5CEP	0.024	0.784	0.005	0.025	0.199	0.064	0.972	0.004	0.311	0.005	2.90	4.10	2.50	1.40	8.30	6.20	103.40	4.40	5.10	40.70	8.40	0.00	3.20
6CEP	0.011	0.446	0.005	0.023	0.116	0.064	1.840	0.015	0.755	0.002	3.30	4.10	2.80	1.00	17.60	5.10	84.00	4.20	3.70	36.30	5.80	3.80	5.30
1CEU	0.004	0.037	0.002	0.012	0.052	0.041	0.076	0.004	0.333	0.002	3.30	4.40	3.10	1.20	6.40	5.10	16.70	5.00	8.20	25.10	13.60	4.10	8.00
2CEU	0.004	0.031	0.001	0.013	0.066	0.037	0.056	0.004	1.430	0.002	2.20	4.30	2.90	1.30	5.70	4.00	17.10	5.20	12.40	24.60	19.80	4.00	8.70
3CEU	0.012	0.039	0.004	0.027	0.068	0.045	0.099	0.004	0.785	0.002	2.20	4.60	2.70	1.30	5.90	4.30	17.20	5.60	8.30	29.00	10.70	4.20	3.50
4CEU	0.004	0.024	0.003	0.009	0.046	0.027	0.069	0.004	0.671	0.002	3.60	4.90	2.70	1.50	8.10	5.10	45.20	5.20	11.50	35.60	10.40	4.20	6.10
5CEU	0.025	0.040	0.001	0.015	0.066	0.034	0.027	0.004	0.577	0.002	3.40	4.00	2.40	0.90	4.90	5.30	36.00	4.40	5.70	26.10	10.30	3.90	4.40
6CEU	0.013	0.066	0.015	0.071	0.064	0.035	0.106	0.004	1.269	0.004	3.30	7.60	3.40	3.30	7.60	5.80	20.50	4.90	5.70	27.50	16.30	4.20	1.30

Rioja). The results for elemental contents of leaves (CEH), petioles (CEP) and grapes (CEU) are also included in Tab. 3 and follow the corresponding plot number.

Major and trace elements are presented together, even if their concentrations differ in magnitude (the former are represented as percentages and the latter in ppm), in order to elucidate their potential interactions as these could not be compared readily on using the same order of magnitude to measure concentrations. These two parameters have been used together to ascertain the origin of other products such as potatoes (Casañas *et al.* 2003, Di Giacomo *et al.* 2007). The average and standard deviations of the total contents are represented in Tab. 4.

In the case of major elements we detected that the contents of Si, Al and Ca are predominant for the soils in the region. These results are as expected given the mineralogical characterisation of the studied soils (De la Horra *et al.* 2008, Carlevalis 1992). The macronutrients are found in suitable concentrations for nutrition of the plants (Wild 1992). One exception is the case of K, which has a lower concentration than the average found in the soils of the region (0.82 %), mainly when the results are compared with those for soils from granitic regions (Hugget 2006). The Ca/Mg and Ca/K ratios are high and they can result in absorption problems for Mg and K (Lanyon *et al.* 2004). However, the most frequent problem is ferric chlorosis due to low Fe absorption, which can decrease the productivity even without any evident symptoms (Gruber 2002).

Mn contents are low when presented as an average value (0.065 %) with the exception of plot 4, which contains remnants of volcanic rocks. A high Mn content has been pointed out as being responsible for the particular nature of some wines from Beaujolais (Hugget 2006)

Contents of trace elements in the soil-vine system: The presence of low levels of Zn (41 ppm) and Pb (19 ppm) is inferior as compared to other wine-growing regions such as Champagne (300 ppm and 100 ppm, respectively) (Chopin *et al.* 2008), Oporto (Almeida and Vasconcelos 2003) and other areas that have suffered contamination by spills (Madejon *et al.* 2003).

Data for Cu were not included in Tabs 3 and 4 because results obtained on the soil range from 15 to 20 ppm. However, variations in the Cu content for leaves range from below the limit of detection to 133 ppm, depending on whether the plot has recently undergone fungicidal treatment or not. Significant amounts of Cu were detected when the plots showed symptoms of contamination through treatment (Pohl 2007). In any case, in the studied area, Cu treatments are not frequent and this element does not reach the levels found in other wine-growing regions, which have typical values of around 100 ppm (Almeida and Vasconcelos 2003, Chopin *et al.* 2008).

The particularly high Fe levels found in these soils warrant special mention, even if this element is present in normal proportions (3.8 %) with respect to world soils (Wild 1992) and other soils of La Mancha (Carlevalis *et al.* 1992, De la Horra *et al.* 2008). However, some symptoms of chlorosis were apparent due to the presence of Ca and the high pH of the soil solution (Gruber 2002), a problem that can be especially prevalent if the rootstock

Table 4

Average (X) and standard deviation (S) for major and trace elements. For identification purposes, s is used for soil, h for leaf, p for petiole and u for grape samples. The concentrations are expressed in % for major elements (from Na to K) and in ppm for trace elements (from V to Nd). Bioadsorption levels are represented by Biological Absorption Coefficient (BAC) followed by H for leaf, P for petiole and U for grape

	Xs	Ss	Xh	Sh	Xp	Sp	Xu	Su	BACH	BACP	BACU
Na	0.082	0.026	0.007	0.006	0.025	0.012	0.010	0.009	0.089	0.302	0.126
Mg	0.921	0.130	0.442	0.103	0.619	0.146	0.039	0.014	0.480	0.672	0.043
Al	3.924	1.912	0.055	0.011	0.007	0.002	0.004	0.005	0.014	0.002	0.001
Si	23.886	4.720	0.820	0.276	0.027	0.008	0.019	0.008	0.034	0.001	0.001
P	0.086	0.011	0.179	0.041	0.125	0.044	0.060	0.009	2.078	1.447	0.700
S	0.049	0.010	0.222	0.031	0.075	0.015	0.036	0.006	4.568	1.550	0.751
Ca	9.839	5.110	2.750	0.630	1.693	0.457	0.072	0.029	0.280	0.172	0.007
Mn	0.065	0.022	0.012	0.006	0.005	0.001	0.004	0.000	0.183	0.076	0.060
K	0.829	0.441	0.734	0.315	0.802	0.334	0.844	0.422	0.885	0.967	1.019
Fe	3.839	0.786	0.056	0.013	0.003	0.002	0.002	0.001	0.014	0.001	0.001
V	73.683	20.577	6.933	1.760	4.133	0.924	3.000	0.629	0.094	0.056	0.041
Cr	70.750	18.540	5.183	0.366	4.300	0.167	4.967	1.325	0.073	0.061	0.070
Co	11.983	1.875	2.783	0.440	2.717	0.214	2.867	0.350	0.232	0.227	0.239
Ni	42.933	16.022	2.050	0.423	0.983	0.223	1.583	0.864	0.048	0.023	0.037
Zn	41.917	6.124	15.617	3.435	16.617	6.078	6.433	1.209	0.373	0.396	0.153
Rb	56.100	11.930	3.917	0.747	4.933	1.181	4.933	0.665	0.070	0.088	0.088
Sr	190.217	90.336	133.550	65.579	118.817	52.356	28.783	12.162	0.702	0.625	0.151
Nb	17.883	4.377	4.250	0.524	4.100	0.498	5.050	0.399	0.238	0.229	0.282
Cs	4.267	1.360	5.450	1.111	5.267	2.675	9.133	2.272	1.277	1.234	2.141
Ba	287.383	29.603	39.483	5.191	39.833	5.200	27.983	4.064	0.137	0.139	0.097
Ce	63.800	11.941	10.767	4.330	9.267	2.938	13.517	3.879	0.169	0.145	0.212
Pb	19.667	3.184	3.550	1.763	2.417	1.610	4.100	0.126	0.181	0.123	0.208
Nd	29.083	6.443	4.300	2.862	5.033	1.694	5.333	2.812	0.148	0.173	0.183

is not chosen appropriately (Wooldridge 2010). The Ba/Sr ratio is displaced due to the abundance of Sr in the limestone soils of La Mancha (Conde *et al.* 2009) and because the content of Ba is low compared with the average for world soils (Kabata-Pendias 2001). Sr is of special interest because it can replace the Ca in many physiological and structural features due to the similar ionic radius of these elements (Rollingson 1993).

The abundance of Ni is relatively high, at 43 ppm, without reaching levels of contamination (Reinmann 2001).

Rare earth elements (REE) are also present and particularly abundant are Ce (64 ppm) and Nd (29 ppm). The La content is around 30 ppm, showing low levels of amount in the plant and, for that reason data were not shown in Tab. 3. Other trace elements such as V, Cr and Co are at normal or low levels. The content of Rb is particularly low. This element is characteristic of granitic areas (Almeida and Vasconcelos 2003, Hugget 2006). The behaviour of Rb is of interest as it can replace the K in physiological functions as these elements have a similar ionic radius (Rollingson 1993).

In relation to the content of trace elements in the plant, it can be stated that there are very few global references, although major elements and micronutrients have been widely studied (Lanyon *et al.* 2004, White 2009). The contents of the different elements found in vines of the studied region, when compared to other plants referred in the bibliography (Kabata-Pendias 2001), can be summarized as follows:

- Similar contents: Ca, K, Mg, Ba, Cu, Mn and Ni
- Higher contents: P, S, Co, Cr and V
- Lower contents: Na, Pb and Zn.

It can be observed from the results in Tab. 3 that certain elements accumulate in the plant, e.g. Cs (Kabata-Pendias 2001). The role of fungi in the uptake of nutrients (White, 2009) has been pointed out for elements such as P (Kabata-Pendias 2001, White 2009) in the active participation of the absorption and mobilization of trace elements (Campos *et al.* 2009). This pattern was not found in our case for Rb (low content in the studied soils) or Cd (not detected by the analytical technique used). We agree in pointing out elements that are very weakly uptaken as Zr, Sc, Fe and Al (Kabata-Pendias 2001). However, the Ba content showed a relatively high level in our plots.

Regarding the published foliar analysis data for evaluating the nutritional status of the vine (Wild 1992, 2009 Lanyon *et al.* 2004), all elements obtained in our study are within the limits that are considered normal, with the exceptions of K (0.7 %) and Zn (15 ppm), which are present at relatively low levels without reaching deficiency. In other regions, such as the Douro in Portugal (Pessanha *et al.* 2010), similar results for leaves were obtained in K, Ca and Fe, higher levels in Cu, Zn and Rb and lower levels in Sr. In the Champagne region, Chopin *et al.* (2008) twice the amount of Zn in leaves and very similar contents for Pb in comparison to our study.

The contents of different elements in leaves and petioles are shown in Tab. 3 and it can be observed that the contents are similar for the trace elements. The major elements do show some differences, for example in Na, where the content is higher in petiole, and in Al, Si, Ca, S, Ca, Mn and Fe, which show lower values in petioles than in leaves. Several differences could also be detected in some major elements (P, K, Ca and Mg) depending on the variety and rootstock (Wooldridge 2010).

According to the results in Tab. 3, the contents for the different elements in the fruit are always lower than in the leaves, except for K, since the accumulation of this element is reported to increase as the fruit ages (White 2009).

On the other hand, the contents of some trace elements could enable differentiation of the origin of products, in keeping with other trace and major elements described in the bibliography that could be of interest in relating the plant with the soil of provenance (Ba, Cr, Li, Rb, Sr, Ca, Mg, Mn and Na) (Casañas *et al.* 2003, Kment *et al.* 2005, Pohl 2007, Di Giacomo *et al.* 2007, Almeida and Vasconcelos 2003, Galgano *et al.* 2008).

In the Douro region (Portugal), Pessanha *et al.* (2010) obtained similar results in cultivars for K, Fe and Zn, higher levels for Cu and Rb and lower levels for Ca and Sr. The contents obtained for trace elements are very low in comparison to other regions and species, particularly if the soil suffered some contamination (Reinmann 2001, Madejon 2003).

Bioaccumulation of elements: The level of bioaccumulation was calculated as the ratio between the concentration of any studied element in the leaf, petiole or grape of the vine and the concentration found in the corresponding soil. The capacity of a plant to uptake nutrients is measured as the ratio of the element in the plant and its concentration in the soil. This ratio is called the Biological Absorption Coefficient (BAC), Index of Bioaccumulation (BA) or Transference Factor (TF) (Kabata-Pendias 2001).

BAC values for the vines and the studied soils are shown in Tab. 4. Comparison of the values obtained for leaves with the values obtained from the literature (Kabata-Pendias 2001) allows the following conclusions to be drawn for the different major and trace elements accumulated in the different parts of the vines:

- Values obtained for the major elements that are higher than or close to 1: S (4.56), P (2.07) and K (0.88 in leaf, 0.96 in petiole and 1.01 in grape). In the case of Cs, the values are 1.2 in the leaves and petiole and 2.1 in the fruit.

- Values obtained for different elements in the range 0.1 to 1. This group includes Mg (0.48 in leaves and 0.67 in petiole), Ca (0. 28) and Mn (0.13) amongst the major elements. Trace elements belonging to this class are Sr (0.70), Zn (0.37), Nb (0.23), Co (0.23), Pb (0.18), Ce (0.17), Nd (0.14) and Ba (0.14).

- Values obtained for different elements in the range 0.01 to 0.1. The major elements in this group with low BAC values are: Na (0.08), Al and Fe (0.01) and Si (0.03). The trace elements included in this group are V (0.09), Cr and Rb (0.07) and Ni (0.03).

Peculiarities in the BAC values for the vine, in comparison to other plants, include the high affinity for Sr (the studied calcareous soils are very rich in this element) and for Fe, Ba and rare earth elements. In contrast, the vine has a very low affinity for Rb (very low content in the studied soils) and for Ni and Pb, both of which are present at very low levels in the studied plots.

The BAC values in the leaves are very similar to those obtained in the petiole and are higher than the average values for the grape in all cases.

Correlation between elemental concentration in soil and plant: Having described the average levels of bioaccumulation for each element, we attempted to establish a model for the behaviour of each particular element obtained in this study. This was achieved by comparing the different concentrations of elements in the soils, leaves and grapes. In general, a trace element (whether essential or not) will be accumulated in the plant according to a sigmoid-type function as its concentration in the soil is increased (Kabata-Pendias 2001).

We are aware that the number of plots used for the area is too low to establish general laws for the region. However, one of the objectives of the present study was to outline general trends in order to guide future studies on the behaviour of vines cultivated in our region for each trace element. In this sense, we established simple linear correlations (White 2009) between the content of each element in the soil and its contents in leaf and grape in vines.

The results are shown in Tab. 5. In most cases, the correlations are positive but not significant. Significant correlation does occur in leaf values for Mg, K, V, Cr, Sr and Ce, whereas for grapes the only positive and significant correlation was obtained for Sr.

We appreciate that the significant correlations for Sr and Cr are similar to those obtained for other elements such as P (White 2009) and Hg in woody species (Molina *et al.* 2006). In contrast, in the case of Zn it seems that a definite pattern is not obtained, as shown by the low concentration models for unpolluted soils (Madejón *et al.* 2003). The behaviour for Sr, Zn and Cr for the soil-leaf system is represented in Fig. 2 and in all cases a positive increasing correlation is observed.

As an example of accumulation in the fruit, we can highlight the case of Sr in Fig. 3, which again shows a positive and significant correlation.

Conclusions

From the results obtained in this study it can be concluded that novel and relevant information about the behaviour of vines cultivated in Campo de Calatrava (Subregion of La Mancha- Spain) has been obtained. The results show that the plants accumulated elements in different parts depending on the geochemical properties of the soils. This is especially evident in the case of trace elements, the presence or absence of which could show soil provenance and act as a geochemical fingerprint for the fruit. This study could be important for the chemical identification of wines produced in this region. The studied plots are representative of the area and are varied in their composition. The

Table 5

Correlations between different trace and major elements in the soil-leaf system and soil-grape system, respectively. (*significant correlation is indicated in bold characters)

System	Mg	P	S	Ca	Mn	Fe	K	V	Cr	Al	Si
Soil-leaf	**0.73**	0.53	-0.52	0.67	0.08	**-0.02**	**0.92**	**0.82**	**0.85**	0.49	-0.23
Soil-grape	0.37	0.51	-0.34	0.44	0.01	-0.37	-0.16	-0.20	-0.13	-0.27	-0.52
	Pb	Co	Ni	Zn	Sr	Nb	Cs	Ce	Nd	Na	
Soil-leaf	0.54	0.10	0.46	0.03	**0.78**	0.38	**-0.95**	**0.80**	0.64	-0.19	
Soil-grape	0.01	-0.10	0.07	0.42	**0.97**	0.57	-0.15	-0.26	-0.08	-0.07	

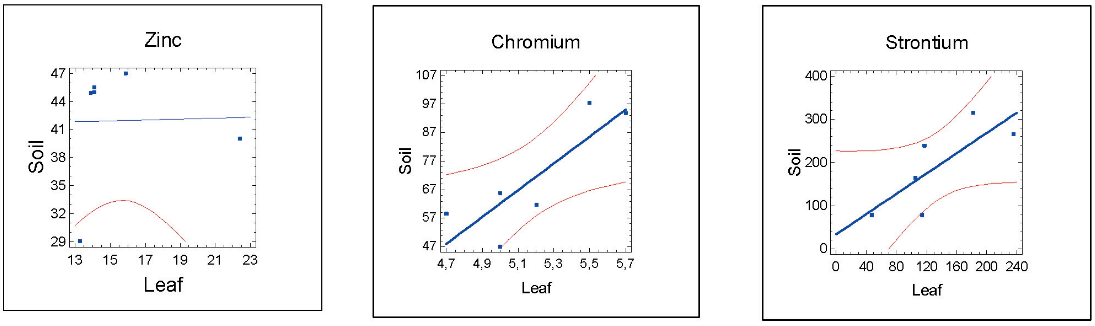

Fig. 2: Correlation between soil and leave contents for Zn, Cr and Sr (from left to right).

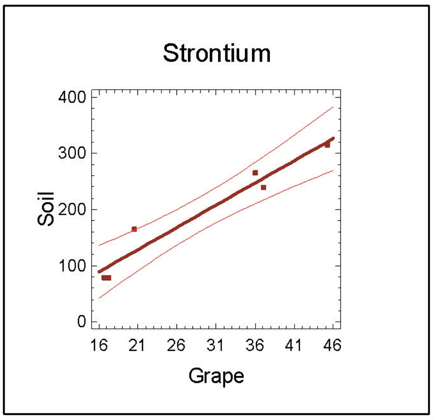

Fig. 3: Correlation of Sr content in grape and soil.

main characteristics are high contents of Ca, Sr, Ni and REE (La, Ce and Nd), low contents of Al, Zr, Ba, Cu, Zn and Pb, and normal contents of the rest of the elements detected.

The contents of elements in the leaves of the vine variety studied (Cencibel) are comparable to the values found in the literature for major elements. Detectable trace elements include Cr, Zn, Rb, Sr, Cs, Ba, Ni, V and Ce and these are of great interest as they could represent a geochemical fingerprint for the plant.

BAC levels are similar to those reported for other plants in other parts of the world. BAC values of interest, with respect to detectable trace elements with the analytical technique used, are Sr (0.70), Zn (0.37), Nb (0.23), Co (0.23), Pb (0.18), Ce (0, 17), Nd (0.14) and Ba (0.14). Elements with very low concentrations, *i.e.* below 0.1, are Al, Fe, V, Cr, Rb and Ni. Furthermore, the plant response to soil elements showed a significant positive linear correlation for V, Cr, Sr and Ce in leaves. For the grape, however, the only element that showed identical behaviour was Sr.

Nonetheless, further research is recommended in order to deeply study the elemental relationship between soil and vines of La Mancha region, evaluating more plots and using higher sensitive analytical techniques for some elements, such as ICP-plasma, to show a more adjusted geochemical fingerprint in the fruits.

Acknowledgements

This work has been done with the support of the Regional Government of Castilla-La Mancha (Spain), project PPII10-0063-8230.

Reference

Almeida, C.; Vasconcelos, M.; 2003: Multielement composition of wines and their precursors including provenance soil and their potentialities as fingerprints of wine origin. J. Agric. Food Chem. **51**, 4788-4798.

Amorós, J. A.; Garcia, F. J.; Sanchez, C. J.; Marquez, E.; Bravo, S.; Jimenez, R.; 2008: Main viticole soils in Castilla-La Mancha. Proc. VII[th] Int. Terroir Congr. Nyon (Switzerland).

Amorós, J. A.; Pérez de los Reyes, C.; Garcia, F. J.; Sanchez, C. J.; Jimenez, R.; 2010: Description of red soils in a semiarid climate and evaluation for vineyard (*Vitis vinifera* L.) use. Fresenius Environ. Bull. **19**, 1199-1207.

Atalay, I.; 1997: Red Mediterranean soils in some karstic regions of Taurus mountains, Turkey. Catena **28**, 247-260.

Barbaste, M.; Medina, B.; Sarabia, L.; Ortiz, M. C.; Pérez-Trujillo, J. P.; 2002: Analysis and comparison of SIMCA models for denominations of origin of wines from de Canary Islands (Spain) builds by means of their trace and ultratrace metals content. Analyt. Chim. Acta **472**, 161-174

Bronger, A.; Sedov, S.; 2003: Vetusols and paleosols: natural versus man induced environmental change in the Atlantic coastal region of Morocco: Quaternary Int. **106-107**, 33-60.

Campos, J. A., Tejera, N. A., Sánchez, C. J.; 2009: Substrate role in the accumulation of heavy metals in sporocarps of wild fungi. Biometals **22**, 835-841.

Carlevalis, J. J.; De La Horra, J. L.; Serrano, F.; Rodriguez, J.; 1992: La fertilidad de los principales suelos agrícolas de la zona oriental de la provincia de Ciudad Real. La Mancha y Campo de Montiel. C.S.I.C. and J.J.C.C. Castilla-La Mancha, Vol. 1.

Casañas, R.; Suárez, P.; Rodriguez, E.; Darias, J.; Díaz, C.; 2003: Mineral concentrations in cultivars of potatoes. Food Chem. **83**, 247-253.

Conde, P.; Martín, J.; De la Horra, J.; Jiménez-Ballesta, R.; 2009: Trace elements contents in different soils of a semiarid mediterranean environment: Castilla-La Mancha, Spain. Fresenius Environ. Bull. **18**, 858-867.

Chopin, E. I. B.; Marin, B.; Mkoungafoko, R.; Rigaux, A.; Hopgood, M. J.; Delannoy, E.; Cance`s, B.; Laurain, M.; 2008: Factors affecting distribution and mobility of trace elements (Cu, Pb, Zn) in a perennial grapevine (*Vitis vinifera* L.) in the Champagne region of France. Environ. Pollution **156**, 1092-1098.

De La Horra, J. L.; Serrano, F.; Carlevalis, J. J.; 2008: Estudio de suelos del Campo de Calatrava (Ciudad Real) y sus condiciones de fertilidad. C.S.I.C., Vol. 32.

Di Giacomo, F.; Del Soignore, A.; Giaccio, M.; 2007: Determining the Geographic Origin of Potatoes Using Mineral and Trace Elements Content. J. Agric. Food. Chem. **55**, 860-866.

Drouineau, G.; 1942: Dosage rapide du calcaire actif de sols. Ann. Agron. **12**, 441-450.

FAO ISRIC ISSS; 2006: World reference base for soil resources. A framework international classification, correlation and communication. World soil resources report 103, FAO, Rome.

Fiket, Z.; Mikac, N.; Kniewald, G.; 2011: Arsenic and other trace elements in wines of eastern Croatia. Food Chemistry **126**; 941-947.

Galani-Nikolakaki, S.; Kallithrakas-Konto, N.; Katsanos, A. A.; 2002: Trace elements analysis of Cretan wines and wine products. Sci. Total Environ. **285**, 155-163.

Galgano, F.; Favati, F.; Caruso, M.; Scarpa, T.; Palma, A.; 2008: Analysis of trace elements in southern Italian wines and their classification according to provenance. Food Sci. Technol. **41**, 1808-1815.

García, F. J.; Amorós, J. A.; Sánchez, C.; Jiménez-Ballesta, R.; 2009: Red soil geochemistry in a semiarid mediterranean environment and its suitability for vineyards Actas VII Congreso Ibérico de Geoquímica, 315-324.

García, J. M., Santos, F.; 1997: Relationship between the characteristics of Mediterranean Red soils and the age of the geomorphological surfaces in central-western Spain. Catena, **28**, 231-245.

Gee, G. W.; Bauder, J. W.; 1986: Particle-Size Analysis. In: A. Klute (Ed.): Methods of Soil Analysis. Part 1. Physical and Mineralogical Methods, 2nd Ed. Agronomy Monograph **9**, 383-411. ASA-SSSA, Madison.

Gonzálvez, A.; Llorens, A.; Cervera, M. L.; Armenta, S.; de la Guardia, M.; 2009: Elemental fingerprint of wines from the protected designation of origin Valencia. Food Chem. **112**, 26-34.

Gruber, B.; Kosegarten, H.; 2001: Depressed growth of non chlorotic vine grown in calcareous soil is an iron deficiency symptoms prior to leaf chlorosis. J. Plant Nutr. Soil Sci. **165**, 111-117.

Hidalgo, L.; 1980: Caracterización Macrofísica del Ecosistema Medio-Planta en los Viñedos Españoles. I.N.I.A. Comunicaciones, Vol. 29.

Hugget, J. M.; 2006: Geology and wine: a review. Proc. Geolog. Assoc. **117**, 236-247.

Kabata-Pendias, A.; 2001: Trace Elements in Soils and Plants, 3rd ed. CRC Press, Boca Raton.

Kment, P.; Mihaljevic, M.; Ettler, V.; Sebek, O.; Strnad, L.; Rohlova, L.; 2005: Differentiation of Czech wines using multielement composition - A comparison with vineyard soil. Food Chem. **91**, 157-165.

Kwan, W. O.; Kowalski, B. R.; Skogerboe, R. K.; 1979: Pattern recognition analysis of elemental data. Wines of *Vitis vinifera* cv. Pinot Noir from France and the United States. J. Agric. Food Chem. **27**, 1321-1326.

Lanyon, D.; Cass, A.; Hansen, D.; 2004: The Effect of Soil Properties on Vine Performance CSIRO Land Water Techn. Rep. 34/04.

Madejón, P.; Murillo, J. M.; Marañón, T.; Cabrera, F.; Soriano, M. A.; 2003: Trace element and nutrient accumulation in sunflower plants two years after the Aznalcóllar mine spill. Sci. Total Environ. **307**, 239-257.

Molina, J. A.; Oyarzum, R.; Esbrí, J. M.; Higuera, P.; 2006: Mercury accumulation in soils and plants in the Almadén mining district, Spain: one of the most contaminated sites on Earth. Environ Geochem. Health **28**, 487-498.

Nelson, D. V., Sommers, L. E.; 1982: Total carbon, organic carbon and organic matter. In: A. L. Page, R. H. Miller, D. R. Keeney (Ed.): Methods of soil analysis: Part 2, Chemical and microbiological properties, 2nd ed. Madison, WI: Amer Soc Agron, 539 -579.

Munsell Color Co.; 1998: Munsell Soil Color Charts. Munsell Color Co., Nueva York.

Ortiz, I.; Simón, M.; Dorronsoro, C.; Martín, F.; García, I.; 2002: Soil evolution over the Quaternary period in a Mediterranean climate (SE Spain). Catena **48**, 131-148.

Paneque, P.; Alvarez-Sotomayor, M. T.; Gómez, I. A.; 2009: Metal contents in "oloroso" sherry wines and their classification according to provenance. Food Chem. **117**, 302-305.

Paneque, P.; Alvarez-Sotomayor, M. T.; Clavijo, A.; Gómez, I. A.; 2010: Metal content in southern Spain wines and their classification according to origin and ageing. Microchem. J. **94**, 175-179.

Pessanha, S.; Carvalho, M. L.; Becker, M.; Von Bohlen, A.; 2010; Quantitative determination on heavy metals in different stages of wine production by Total Reflection X-ray Fluorescence and Energy Dispersive X-ray Fluorescence: Comparison on two vineyards. Food Chem. **112**, 26-34.

Pillet, F.: 2007; Geografía de Castilla-La Mancha. ISBN: 978-84-35-656-0-2.

Pohl, P.; 2007: What do metals tell us about wine? Trends Analyt. Chem. **26**, 941-949.

Rollinson, H.; 1993: Using Geochemical Data: Evaluation, Presentation, Interpretation. Pearson Ed. Ltd.

SCS-USDA; 1972: Soil Survey Investigations Report No. 1. Soil Survey Laboratory Methods and Procedures for Collecting Soil Samples. US Govt. Printing Office, Washington.

Serapinas, P.; Venskutonis, P. R.; Aninkevičius, V.; Ežerinkis, Ž.; Galdikas, A.; Juzikiené, V.; 2008: Step by step approach to multi-element data analysis in testing the provenance of wines. Food Chem. **107**, 1652-1660.

Wild, A.; 1992: Condiciones del Suelo y el Desarrollo de las Plantas según Russell. Ed. Mundiprensa.

White, R. E.; 2009: "Understanding Vineyard Soils". Oxford University Press. ISBN: 978-0-19-531125-9.

Wooldridge, J.; Louw, P. J. E.; Conradie, W. J.; 2010: Effects of rootstock on grapevine performance, petiole and must composition, and overall wine score of *Vitis vinifera* cv. Chardonnay and Pinot Noir. S. Afr. J. Enol. Vitic. **31**, 45-48.

Yaalon, D.H.; 1997: Soils in the Mediterranean region: what makes them different? Catena **28**, 157-169.

Yassoglou, N.; Kosman, C.; Moustakas, N.; 1997: The red soils, their origin, properties, use and management in Greece. Catena **28**, 261-278.

Received September 16, 2011