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Grapevine leaf uptake of mineral elements influenced by sugar foam amendment of an acidic soil

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Summary

The use of sugar foam (industrial waste from sugar beet extraction) as an acidic soil (raña) liming agent has been studied in a singular winegrowing region. The contents of the major elements (Al, Ca, Fe, K, Na, Mg, S, Si) and trace elements (As, Ba, Ce, Co, Cr, Cs, Cu, Ga, Hf, La, Mo, Nb, Nd, Ni, Pb, Rb, Sc, Sn, Sr, Ta, Th, U, V, W, Y, Zn, Zr) in the original soil, the amended soil and in grapevine leaves has been measured by X-ray fluorescence. The addition of sugar foam modified the agronomic properties of the original soil. The amendment caused a slight increase in major elements (Ca, 10.4 $g \cdot kg^{-1}$; Mg, 1.9 $g \cdot kg^{-1}$ and K, 12.9 $g \cdot kg^{-1}$) and decreased Al (from 62 to 57.8 $g \cdot kg^{-1}$) and Fe (from 41.2 to 26.5 $g \cdot kg^{-1}$) content. Regarding trace elements, there was an increase in levels of Ba, Rb and Sr in the amended soil in comparison to the original soil. The major elements that accumulated in the vine leaf were Ca, Mg and S (Biological Absorption Coefficient, BAC, greater than 1). As for trace elements in leaf, Ba and Sr had a "medium" BAC (0.27 and 0.8, respectively) whereas Rb had a "slight"value (0.08). It is worth noting that the bioaccumulation rate of Zn was greater than 1. The use of sugar foam as a liming agent did not have a negative effect on the absorption of major and trace elements in vine leaves and led to improved BAC values for essential elements in the grapevine. The treatment did not increase the amount of trace elements in the soil above the reference levels for the region.

K e y w o r d s : Biological Absorption Coefficient (BAC), pH, liming, trace elements, reference levels.

Introduction

Soil acidity can be a serious problem in agriculture. In order to correct this problem, calcium and magnesium compounds are added to the soil and this raises the pH and significantly changes other properties. As a result, this contribution is considered to be a soil amendment (Urbano 1999). Among the products used as liming materials, industrial wastes such as sugar foam can be employed and this product is registered in the Spanish regulations (Garrido *et al*. 2003).

Sugar foam is the residue obtained from the manufacture of sugar. The material is rich in organic matter (around 7 %) and calcium carbonate (approximately 40 %) (Azucarera Ebro 2005, Villa 2005, Jiménez-Moraza *et al*. 2006) and this composition allows it to be applied as a liming agent. In Spain, however, only a low percentage of sugar foam is used for liming when compared to other European countries, in which almost their entire production is applied to cultivated soils (López *et al*. 2001, Jiménez-Moraza *et al*. 2006).

The vine, like other crops, is affected by soil pH. Excellent wines can be produced from grapevines grown on acidic soils, although the recommended pH (KCl) for vines is between 5.5 and 7.5 (White 2009). For this reason, if a soil is acidic it is often amended before planting in order to raise the pH. After liming, the study of the physical, chemical and geochemical soil properties supports fertility and the availability of plant nutrients. The major elements provide details of structural components and potential nutrients (Wild 1992, White 2009) and the trace elements content provides information about soil geochemical background (García Navarro *et al*. 2009) and toxicities (Kabata-Pendias 2004, Jiménez-Ballesta *et al*. 2010). Natural values of potential pollutants ("background levels") are used to establish "reference values" that indicate the limit below which there is no environmental risk (Jiménez-Ballesta *et al*. 2010). Trace and major elements may have synergistic or antagonistic interactions and be beneficial or toxic depending on their concentrations (Kabata-Pendias 2001). These interactions mean that liming does not always produce the expected effect in terms of the uptake of trace elements by plants (Tyler and Olsson 2001, Kabata-Pendias 2004). Although the metabolism of trace elements in plants has been studied by several authors (Wild 1992, Kabata-Pendias 2001, Tyler and Olsson 2001), there are very few references concerning the contents of these elements in vine leaves (Chopin *et al*. 2008, Pessanha *et al*. 2010, Amorós *et al*. 2012a, 2012b). However, the presence of these elements has been more widely studied in grapes (Rogiers *et al*. 2006, Bertoldi *et al*. 2009, 2011, Amorós *et al*. 2012b) and wines (Almeida and Vasconcelos 2003, Marengo and Aceto 2003).

In Castilla-La Mancha (Spain) the traditional soils used for growing grapes are classified as Cambisols or Calcisols (on calcareous materials) and Regosols (without diagnostic horizon) (Amorós *et al*. 2010). Regional refer-

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ence values are based on data obtained mainly from these types of soils (Jiménez-Ballesta *et al*. 2010). In this paper, however, three profiles located in a "raña" (piedmont deposits associated with quartzite on large flat platforms) were explored. "Raña" soils are less frequently used in the region for growing grapes and they often have strong acidity (pH < 5), high weathering, a high proportion of aluminum in the exchange complex and deficiencies in phosphorus, calcium and potassium, all of which cause serious problems for agricultural use (Villa 2005). This restriction has been traditionally solved by liming.

The first objective of the work described here was to study the effects that sugar foam, used as a liming agent, has on acidic vineyard soil properties and to obtain information about the major and trace elements present in the original and amended soils. The second objective was to determine which of these elements are present in grapevine leaves in significant quantities.

The interest in this study is that the soil was modified on the basis of agronomic and commercial criteria to improve the agro-soil-plant system and thus satisfy the needs of the winemaker.

Material and Methods

Location and climatic characteristics: The experiment was carried out on three "raña" profiles located in Retuerta del Bullaque (Ciudad Real, Castilla-La Mancha, Spain). Profiles, which were a short distance from each other, were located at different altitudes (839 m, 822 m and 804 m for profiles 1, 2 and 3 respectively). The plots were used for the cultivation of grapevines and belonged to Pago de Vallegarcía, a vineyard of 31 ha belonging to the region of Montes de Toledo (Fig. 1). The vineyard was located at the entrance to the farm in

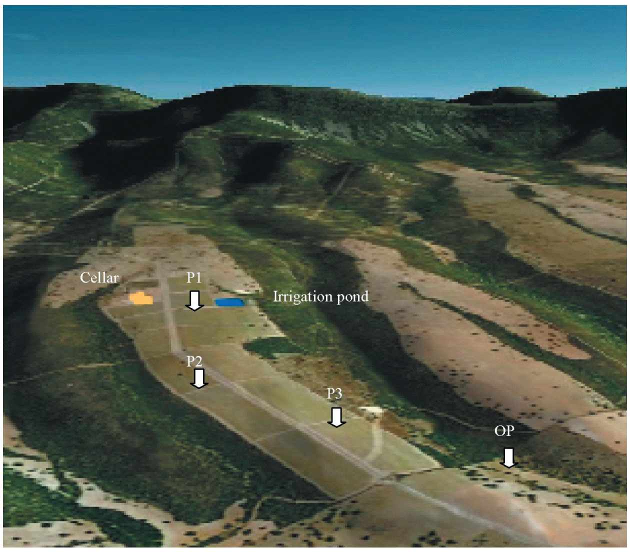

Fig. 1: Overview of the Vallegarcía farm (Ciudad Real, Spain) and soil and vine leaf sampling areas: P1 (Profile 1, 'Cabernet Franc'), P2 (Profile 2, 'Merlot'), P3 (Profile 3, 'Cabernet Sauvignon') and OP (original profile, natural vegetation, original picture from the Vallegarcía property).

14 plots along the access road to the property. The profiles were opened on the plots of 'Cabernet Franc' (P1), 'Merlot' (P2) and 'Cabernet Sauvignon' (P3). All varieties were conducted in Smart-Dyson system, with spur pruning and cover crop between rows.

The local climate is continental, with hot/dry summers and cool/wet winters and an average annual rainfall of 622 mm. According to the climate classification of Köppen-Geiger, the climate type is "temperate", Csa (AEMET 2011).

In the vineyard soil, 10 $t \cdot ha^{-1} \cdot year^{-1}$ of sugar foam were deposited during the years 2003-2006 by ploughing (40 cm). The sugar foam was provided by the Spanish producer Azucarera Ebro SL, which marketed it as an amendment under the name Carbocal (Azucarera Ebro 2005).

In March 2011 the three profiles (P1, P2 and P3) were opened with a backhoe. The profiles were described according to the criteria of the FAO (2006). Samples were subsequently taken from each horizon, air-dried and sieved (< 2 mm) prior to analysis in the laboratory. A sample from the surface horizon of the original soil (OP) under natural climax vegetation and without tillage or amendment with sugar foam was taken, dried and sieved for analysis.

In August 2011, a sample of 20 grapevine leaves was taken from each plot, all from similar positions, with optimal health status and similar age (White 2009). The leaf blades were dried in an oven (7 d at 40 °C), milled, labeled and stored.

Analytical methods: The laboratory tests were carried out according to SCS-USDA (1972). The soil texture was determined using the hydrometer method (Gee and Bauder 1986) and determination of calcium carbonate was carried out with a calcimeter (Porta *et al*. 1986). The organic matter was determined by potassium dichromate oxidation and titration of remaining dichromate with ammonium ferrous (II) sulfate (Anne 1945). The pH was determined with a pH meter in 1:2.5 soil/water solution and 0.1 M KCl solution 1:2.5 (Porta *et al*. 1986). The available phosphorus was determined by the method of Olsen (Olsen *et al.* 1954) and the total nitrogen by the modified Kjendahl method (AENOR 2007). Exchangeable Na, K, Ca and Mg were determined by atomic absorption spectrometry. The method proposed by Schwaiger (2009) was used to determine the cation exchange capacity. All samples were extracted and analyzed in triplicate. The soil samples from surface horizons were hand-milled in an agate mortar and analyzed by X-ray fluorescence to quantify the major components (Al, Ca, Fe, K, Na, Mg, S and Si in $g \cdot kg^{-1}$) and trace elements (As, Ba, Ce, Co, Cr, Cs, Cu, Ga, Hf, La, Mo, Nb, Nd, Ni, Pb, Rb, Sc, Sn, Sr, Ta, Th, U, V, W, Y, Zn and Zr in $mg \cdot kg^{-1}$), both expressed as elements, using a calibration for trace elements in a sequential spectrometer device (Philips Magix Pro with Rhodium anode in the X-ray tube) with a maximum power of 4 kW (set of crystal analyzers for LiF220, LiF200, Ge, PET and PX1, flow detector and twinkle detector). Analysis of the samples was carried out with pearls of lithium borate. Quality control was achieved with analysis of duplicate samples and certified reference material (NIST-2710a for soils and BCR-62 for plants). Leaf blade samples were analyzed by the same method.

Table 1

Soil characteristics of studied profiles (Profile 1, Profile 2, Profile 3 and Original Profile) detailed by horizon. (P is given in mg·kg^{-1} and CEC, Ca^{2+}, Mg^{2+}, Na^{+} and K^{+} are given in cmol·kg^{-1})

Horizon		Depth cm	Color Dry	Color Wet	Clay %	Stoniness %	Texture	pH H_2O	pH KCl	Electrical conductivity dS/m	$CaCO_3$ %	P_2O_5 (Olsen) mg·kg^{-1}	Total N %	Organic matter %	Cations Ca^{2+}	Cations Mg^{2+}	Cations K^{+}	Cations Na^{+}	CEC cmol·kg^{-1}	BS %
Profile 1	A_p	0-31	7.5 YR 5/4	5 YR 3/1	23.6	20	Sandy-Clay-Loam	8.4	8.2	0.05	1.8	16.7	0.042	1.7	18.2	2.1	0.3	1.9	14.6	100
	B_{tg1}	31-67	10 YR 6/8	7.5 YR 5/6	53.6	30	Clay	6.9	5.8	0.05		0.7	0.014	0.7	6.9	1.3	0.3	0.5	33.0	27.4
	B_{tg2}	>67	10 YR 5/8	7.5 YR 5/6	47.6	30	Clay	5.3	4.5	0.03										
Profile 2	A_p	0-33	10 YR 5/6	5 YR 6/4	33.6	40	Clay-Loam	8.9	8.3	0.08	2.0	8.4	0.040	1.7	29.9	2.9	0.2	0.4	8.7	100
	B_{tg1}	33-68	10 YR 6/8	7.5 YR 6/6	43.3	40	Clay	4.8	4.2	0.03		0.1	0.032	1.5	2.1	0.7	0.1	0.4	24.0	13.5
	B_{tg2}	>68	7.5 YR 6/8	7.5 YR 5/6	47.6	40	Clay	4.7	3.9	0.02										
Profile 3	A_p	0-30	10 YR 5/4	5 YR 5/2	33.6	50	Clay-Loam	8.2	7.6	0.08	2.1	16.3	0.070	3.6	18.5	2.1	0.2	0.6	5.9	100
	B_{tg1}	30-62	10 YR 6/8	7.5 YR 6/6	43.6	40	Clay	5.3	4.3	0.02		2.2	0.028	1.0	4.0	0.9	0.2	1.1	38.7	15.9
	B_{tg2}	>62	10 YR 6/8	7.5 YR 5/6	63.6	40	Clay	4.7	4.0	0.04										
Original profile	A				14.5		Loam	5.7	4.9	0.07	1.5	2.97		9.3	6.7	0.3	1.8	0.3	63.1	14.4

CEC.: Cation Exchange Capacity; B.S.: Base Saturation

Results and Discussion

M a c r o m o r p h o l o g i c a l d e s c r i p t i o n o f t h e p r o f i l e s a n d s o i l p r o p e r t i e s: The main characteristics of the studied profiles are summarized in Tab. 1. According to Soil Taxonomy (SOIL SURVEY STAFF 2006), the studied soils were classified as Typic Palexerult ("raña" is usually classified in the order Ultisol) (VIDAL *et al*. 2006).

Regarding textural classes, the topsoil modified by sugar foam shows average values for sand (49.3 %), silt (20.4 %) and clay (30.3 %) that correspond with the sandy-clay-loam textural class, while the original soil has a loam textural class. The values of pH, electrical conductivity (dS/m), organic matter (%) and calcium carbonate (%) of the Vallegarcía soils are also given in Tab. 1. On considering the pH of each profile, the first thing that must be highlighted is the substantial variation in pH between the A and the B horizons in all profiles, with a maximum variation of 4.1 pH units in profile 2 (pH = 8.9 in Ap and pH = 4.8 in Btg1). There is also a variation between the pH of the amended surface horizons (8.5 on average) and the original soil (5.7). This is a direct consequence of the sugar foam amendment (VIDAL *et al*. 2007, OLEGO *et al.* 2012).

It can be seen that the addition of sugar foam does not lead to a variation in the electrical conductivity (0.07 dS·m^{-1} on average in the surface amended horizons and in the original soil), as reported in other studies (GARRIDO *et al.* 2003, GARCÍA NAVARRO *et al*. 2009, PÉREZ DE LOS REYES *et al.* 2011). Levels of $CaCO_3$ (1.9 % on average) and organic matter (2.3 % on average) are suitable for cultivation. The organic matter content of the original soil (9.3 %) is a result of its natural covering vegetation and the lack of tillage.

The cation exchange capacity (CEC) in the sugar foam-amended horizons (average of 9.7 cmol·kg^{-1}) is lower than the CEC of the natural topsoil (63.1 cmol·kg^{-1}). This property is closely related to organic matter content and the percentage of clay (AMORÓS *et al*. 2010, WHITE 2009). The percentage saturation of bases in the amended soil is particularly high (100 %) in comparison to the original acidic soil (14.4 %) because the sugar foam saturates the exchange complex with bases (mainly Ca^{2+}), thus displacing cations such as Al and Mn (VIDAL *et al.* 2006).

The N and P values, which are related to the soil fertility, are suitable for grapevine growth (URBANO 1999). Sugar foam increases the availability of phosphorus in soil (PEREGRINA 2005) and this is reflected in the P_2O_5 values shown in Tab. 1 (P1, P2 and P3 average 13.8 mg·kg^{-1} versus 2.97 mg·kg^{-1} in OP). The technical management of the property reported that they fertilized the vineyard annually by dripping (for NPK) and by leaf (for B and Zn) because of the decrease in the availability of the latter elements at pH > 7 (JACKSON 2008).

Roots are developed in both Ap (many, all sizes) and Bt (common, medium) horizons due to the cover crop between rows system.

M a j o r a n d t r a c e e l e m e n t s i n s o i l: Fig. 2 shows the levels of major elements in the soil modified by sugar foam calculated as the average of the contents of these elements in the surface horizons of the three pro-

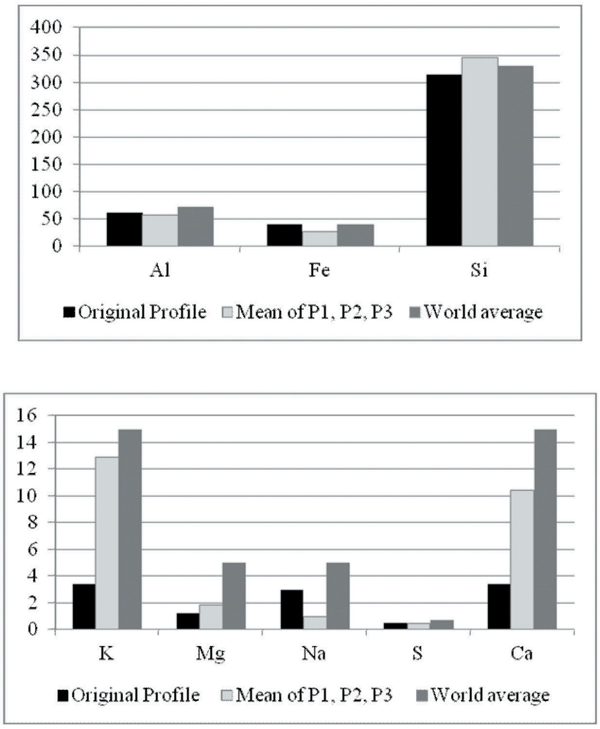

Fig. 2: Major elements (g·kg^{-1}) from the surface horizon of the original profile (OP) of the surface horizons of P1, P2, P3 and global average (SPARKS 2003).

files, the values on the surface horizon of the original soil and the global mean values in surface horizons obtained from SPARKS (2003).

Sugar foams have the aforementioned elements in their chemical composition but the contents vary according to the origin and any industrial process (LÓPEZ *et al.* 2001, VILLA 2005, VIDAL *et al.* 2006). Data for the contents in sugar foam of CaO (270 g·kg^{-1}), K_2O (2 g·kg^{-1}), MgO (12 g·kg^{-1}) and SO_3 (2 g·kg^{-1}) were provided by the supplier (AZUCARERA EBRO 2005), but this material also contains Al_2O_3 (7.3-24.2 g·kg^{-1}), Fe_2O_3 (2.8-1.9 g·kg^{-1}), Na_2O (1-1.05 g·kg^{-1}) and SiO_2 (28.9 to 17.3 g·kg^{-1}) according to data from GARRIDO *et al.* (2003) and PEREGRINA (2005). After the amendment, there was a slight increase in all major elements except for Al (from 62 to 57.8 g·kg^{-1}), Fe (from 41.2 to 26.5 g·kg^{-1} in the original and modified soil, respectively) and Na (3 to 1 g·kg^{-1} in the original and amended soil, respectively). The amended soil contained essential elements for grapevine growth such as Ca (10.4 g·kg^{-1}), Mg (1.9 g·kg^{-1}) and K (12.9 g·kg^{-1}) which, although higher in the amended soil than the original soil as a result of the addition of the sugar foam, are low compared to the global averages (15 g·kg^{-1}, 5 g·kg^{-1} and 15 g·kg^{-1}, respectively). These data are consistent with those reported by VIDAL *et al.* (2006), who observed significant differences in Ca, Al and Fe for the soil treated with sugar foam compared to non-amended soil.

It is interesting to compare the contents of these elements with the content in limy soils of surrounding areas, which are usually dedicated to grapevine cultivation (AMORÓS *et al*., 2012a). The Ca content in the amended soil is far from the values that can be found in surface horizons of calcareous soils (10.4 g·kg^{-1} versus 230 g·kg^{-1}). By contrast, the contents of Si (345.9 g·kg^{-1}) and Fe (26.5 g·kg^{-1}) are much higher in the studied soils in comparison to the traditional vineyard soils of the area (127.5 and 16.65 g·kg^{-1}, respectively). The Al present in the surface horizon of a calcareous soil is around 33.4 g·kg^{-1} while in the original acidic soil the value was 62 g·kg^{-1} and in the same amended soil Al was present at 57.8 g·kg^{-1}.

The contents of trace elements in the surface horizon of the original soil, in the amended profiles and the global average are shown in Tab. 2 (KABATA-PENDIAS 2001, SPARKS 2003). With respect to trace elements, only La, Zr and Hf slightly exceed the reference values proposed by JIMÉNEZ-BALLESTA *et al.* (2010) for Castilla-La Mancha (proposed reference values of 10, 48.4 and 413.1 mg·kg^{-1}, respectively). However, levels found in the amended soil are not considered problematical.

MARENGO AND ACETO (2003) indicated that trace elements can be distinguished whose concentration is affected by the presence of the element in question in the soil or by the vine's ability to uptake it through the roots. These elements include Ba, Mo, Rb and Sr.

In the studied soils, Ba is present at lower levels (188.5 mg·kg^{-1}) than the world average (513.5 mg·kg^{-1}). In calcareous soils, which are the most widely used in viticulture in the region, AMORÓS *et al.* (2012b) reported Ba contents higher (between 242.8 and 317.5 mg·kg^{-1}).

Mo is considered to be an essential micronutrient for the production of grapes (WHITE 2009). The global average value of Mo in soil is 1.1 mg·kg^{-1} (KABATA-PENDIAS, 2001, SPARKS 2003) and the content in the soils under investigation can therefore be considered low (below Low Limit Detection). It is known that the solubility and activity of Mo depends on the pH: at pH values between 3 and 6 the solubility of Mo is low and its activity increases with increasing pH (WHITE 2009). AMORÓS *et al*. (2012a) reported values of 1.22 mg·kg^{-1} for Mo in calcareous soils of Castilla-La Mancha (Spain) with a pH of 8.

The content of Rb in mineral soils strongly depends on inherited minerals from the parent rock, quartzite in this case, with global averages about 111.5 mg·kg^{-1}. Both the original and the amended soils have lower Rb contents than the world average (42.9 mg·kg^{-1} and 49 mg·kg^{-1}, respectively) but these are higher than the values reported by AMORÓS *et al*. (2012a) in calcareous soils (40 mg·kg^{-1}). The behavior and ionic radius of Rb^+ is similar to that of K^+ (ROLLINSON 1993) so that the initial low content in K leads one to expect a low content in Rb, which increases as a result of the increase in the soil pH.

Finally, Sr has values of 61.2 mg·kg^{-1}, 68.7 mg·kg^{-1} and 220 mg·kg^{-1} for the original soil, amended soil and world average, respectively. In other vineyard areas, such as Porto, Sr levels detected in soil are also low, with a value of 20 mg·kg^{-1} (ALMEIDA AND VASCONCELOS 2003). However, in calcareous soils of Castilla La Mancha the average content of Sr is high (about 260 mg·kg^{-1}) (AMORÓS *et al*. 2012a) and in non-limestone vineyard soils of the region the level is around 79 mg·kg^{-1} (AMORÓS *et al*. 2012b). Sr^{2+} has a behavior and ionic radius similar to those of Ca^{2+} (ROLLINSON 1993) and, as a result, in acidic soils high levels of this

Table 2

Trace element contents (in alphabetical order) in mg·kg^{-1} in the surface horizon of the studied soils and global averages

Element	Original Profile (mg·kg^{-1})	Mean P1, P2, P3 ± Standard deviation (Surface horizon) (mg·kg^{-1})	Low Limit Detection (LLD) (mg·kg^{-1})	Global average (Kabata-Pendias 2001; Sparks 2003) (mg·kg^{-1})
As	4.2	13±5.38	0.06	15.5
Ba	176.4	188.5±21.73	3.86	513.5
Ce	116.7	83.5±10.86	1.33	55
Co	3.7	3.2±0.22	1.91	9
Cr	42	35.8±4.07	0.90	68.5
Cs	3.2	5±1.40	0.11	3.5
Cu	7.5	10.7±2.90	0.07	27
Ga	9.6	8.7±0.95	0.49	18.5
Hf	11	19±1.82	1.53	7
La	58.1	43.5±2.94	2.34	35.5
Mo	< LLD	< LLD	0.52	1.1
Nb	14	14.5±1.56	0.28	13
Nd	49.7	36.4±5.43	3.59	30.5
Ni	7.9	12.7±2.85	0.81	37
Pb	21.1	15.9±1.03	0.06	32
Rb	42.9	49±5.82	0.19	111.5
Sc	8.2	6.6±0.52	1.79	8
Sn	1.9	2±0.34	0.02	4
Sr	61.2	68.7±2.27	0.20	220
Ta	< LLD	< LLD	3.37	3
Th	11.9	15.8±2.38	0.74	8.5
U	2.9	3.5±0.21	1.33	3
V	89.8	71.9±8.48	1.61	95
W	2.9	4.2±0.87	0.12	3
Y	26.2	22.9±2.02	0.31	29
Zn	25.8	23.4±2.18	0.56	78.5
Zr	294.3	451±37.71	0.12	353.5

element are not expected. The low levels of Sr can be considered as a special characteristic of this type of soil.

It is worth highlighting the high levels of Rare Earth Elements (Ce, La and Nd) in both the original (116.7, 58.1 and 49.7 mg·kg^{-1}, respectively) and the amended soil (83.5, 44.5 and 36.5 mg·kg^{-1}, respectively) compared to the global average values (55, 35.5 and 30.5 mg·kg^{-1} respectively).

Major and trace elements in grapevine leaves: The values of major elements (g·kg^{-1}) in leaves of plants of 'Cabernet Franc' (P1), 'Merlot' (P2) and 'Cabernet Sauvignon' (P3) are shown in Tab. 3 along with the mean values in the grapevine, the mean of the amount of major elements in the surface horizon of the studied soil, and the value of the biological absorption coefficient (BAC) (Kabata-Pendias 2001).

The presence of each chemical element in the plant depends on the physical and chemical properties of the soil, the specific capacity of the plant to uptake and accumulate each element individually and, finally, the plant organ that is considered (Kabata-Pendias 2001). Soil pH is one of the main properties that controls the bioavailability of chemical elements and nutrients for plants (Kabata-Pendias 2004, Jackson 2008).

Bearing in mind the categorization proposed by Kabata-Pendias (2001), elements can be classified according to their BAC as "Lack" (Na and Si), "Slight" (Al and Fe), "Medium" (K) and finally "Intensive" (Ca, Mg and S); the latter class has a BAC greater than 1.

López *et al*. (2001) noted that the supply of sugar foam to the soil was reflected in a slight increase in Ca and Mg in the dry leaf matter of legumes and grasses when compared to the contribution of other amendments. This fact would explain the high BAC observed for these elements. The high biological absorption coefficient for S obtained in this study (3.57) is close to the values given by Amorós *et al.* (2012a) of 2.2 and, in the case of grapevines, its presence in the plant is related to crop management (application of fungicides). According to García-Escudero *et al.* (2012), K values in this study are "optimal" (mean of 8.1 g·kg^{-1}) when compared with the levels of nutrients in Tempranillo variety leaves during the period of veraison (between 7.7 and 9.1 g·kg^{-1}). In accordance with the study described by García-Escudero, the levels of Fe are considered "high" (0.4 g·kg^{-1} > 0.2 g·kg^{-1}).

The contents of trace elements are also given in Tab. 3 (only above Low Limit Detection). As indicated by Amorós *et al*. (2012a) in a specific study on the influence of the variety on the content of trace elements, there are no significant differences in the amounts of trace elements depending on the plant variety. For this reason we considered the three varieties to obtain the average values in grapevine plants.

Overall, the Kabata-Pendias (2001) classification was employed and BAC trace elements recorded in this study on grapevine leaves can be divided into "Slight" (0.01-0.1) (Cu, Ga, Hf, Rb, V), "Medium" (0.1-1) (Ba, Ce, Co, Cr, La, Nb, Nd, Pb, Sr, Y) and "Intensive" (> 1) (Cs, Zn). Regarding the latter, Kabata-Pendias (2004) has already indicated that Zn was an element with an "easy" or "moderate" bioavailability depending on the soil pH. This fact is remarkable in grapevine since this element is considered to be an essential micronutrient for cultivation. In the case of Zn, one must also consider that in the usual management of the farm, the element is applied annually by leaves because it is slightly immobile at basic pH. The Zn values recorded (24.4 $mg \cdot kg^{-1}$) are similar to those obtained by Chopin *et al*. (2008) in grapevine leaves in Champagne (France) but they can be considered as low ("low to marginal") for the cultivation of the grapevine (White 2009).

Rare Earth Elements (Ce, La and Nd) have medium BAC values (0.25, 0.29 and 0.21 respectively) that are close to those recorded by Amorós *et al*. (2012a) for grapevine leaves of different varieties grown in a calcareous soil (0.28, 0.23 and 0.31, respectively) and in the order of magnitude of the values given by other authors for forest plants (Tyler 2004).

Ba is not apparently an essential component of the leaf tissue but it is usually present in them. In this case, the BAC is 0.27, *i.e.* higher than the value provided by Kabata-Pendias (2001) for the whole plant (0.001). Amorós *et al*. (2012a) reported an average BAC value for Ba in grapevine growing on limy soil of 0.26, which is close to values obtained in this study and much higher than data for other plants.

Rb, like other monovalent cations, is easily uptaken by plants and thus usually has BAC values above 1. In the leaves of grapevines under investigation the BAC has a low value due to the lack of rubidium in the soil (Tab. 2) and in the plant. In the Douro area in Portugal, Pessanha *et al.* (2010) obtained values of Rb for grapevine leaves of about 10 $mg \cdot kg^{-1}$, *i.e.* higher than those obtained in this study (3.7 $mg \cdot kg^{-1}$), and this may be a reflection in the plant of the soil geochemical composition.

Sr contents in plants are highly variable and depend on vegetative formations. Amorós *et al*. (2012b) found a positive correlation between the amount of Sr in the soil and the amount of Sr in leaf and grape. The value obtained on grapevine leaves in this study (39 $mg \cdot kg^{-1}$) is low, being

Table 3

Major ($g \cdot kg^{-1}$) and trace ($mg \cdot kg^{-1}$) element contents in leaves of grapevines near to the profiles P1, P2 and P3, mean value in the surface horizons of the studied soils and Biological Absorption Coefficient (BAC)

Element	P1 Cabernet Franc	P2 Merlot	P3 Cabernet Sauvignon	Mean P1, P2, P3 in grapevine	Mean P1, P2, P3 in surface horizons	Biological Absorption Coefficient (BAC)*
Al	0.75	1.59	1.61	1.3	57.8	0.02
Ca	5.86	16.35	19.22	13.8	10.4	1.32
Fe	0.17	0.55	0.39	0.4	26.5	0.01
K	8.36	5.77	10.28	8.1	12.9	0.63
Mg	1.15	4.18	4.11	3.1	1.9	1.69
S	0.80	1.85	2.40	1.7	0.5	3.57
Si	1.79	3.16	0.15	1.7	345.9	0.004
Ba	53.8	52.6	46.2	50.9	188.5	0.27
Ce	18.9	18.8	25.4	21.0	83.5	0.25
Co	1.4	1.4	2.2	1.7	3.2	0.52
Cr	5.5	5.4	5.7	5.7	35.8	0.16
Cs	8.2	10.4	8.1	8.9	5	1.77
Cu	0.3	0.8	0.1	0.4	10.7	0.03
Ga	0.5	0.5	0.5	0.5	8.7	0.06
Hf	2.5	0.6	1.5	1.5	19	0.08
La	14.4	12.6	10.4	12.4	43.5	0.29
Nb	4.3	3.3	3.9	3.8	14.5	0.26
Nd	8.1	7	7.3	7.5	36.4	0.21
Pb	3.6	3.2	3.2	3.3	15.9	0.21
Rb	3.9	2.7	4.5	3.7	49	0.08
Sr	37.8	42.4	36.9	39	68.7	0.56
V	5.9	7.6	6.3	6.6	71.9	0.09
Y	2.6	2.4	2.4	2.5	22.9	0.11
Zn	17.6	15.3	40.3	24.4	23.4	1.04
Zr	0.6	0.6	0.4	0.5	451	0.001

* BAC: Ratio between the concentration of the element in the plant (leaf blade) and its concentration in the soil (Kabata-Pendias 2001).

similar to leaves of other species and lower than that obtained by Amorós *et al*. (2012a) for other grapevine varieties (Airen, 'Cabernet Sauvignon', 'Cencibel', 'Chardonnay' and 'Garnacha') grown on a calcareous soil (74.9 $mg \cdot kg^{-1}$). The BAC determined in this study for Sr (0.8) is similar to values reported in the scientific literature and it is consistent with moderate bioavailability of the element under aeration conditions and at pH > 5 (Kabata-Pendias 2004).

Conclusions

After an amendment of an acidic vineyard soil with sugar foam, there is a slight increase in all major elements in the soil except for Al and Fe. Ca, Mg and K contents in amended soil are higher than in the original soil. The major elements that accumulate more in the grapevine leaf are Ca, Mg and S, all of which are plant macronutrients, with BAC values above 1. The pH increase obtained by adding sugar foam explains the BAC of Ca (1.32) and Mg (1.69) and the management of the farm explains the BAC of S (3.57). Regarding trace elements, there is an increase in Ba (188.5 $mg \cdot kg^{-1}$), Sr (68.7 $mg \cdot kg^{-1}$) and Rb (49 $mg \cdot kg^{-1}$) in the amended soil with respect to the original. It is worth underlining the high levels of elements classified as Rare Earth Elements (Ce, La and Nd) in both the original soil and the soil amended with sugar foam when compared to global averages. Trace elements in leaves show medium BAC values for Ba (0.27) and Sr (0.8) and a slight value for Rb (0.08). The BAC is greater than 1 for Zn.

Trace element values that are associated with potential toxicity in soils were not found. The application of sugar foam as a liming agent for vineyard soils is strongly recommended due to the known advantages of such treatment (pH above 8, low electrical conductivity of around 0.07 $dS \cdot m^{-1}$ or high organic matter about 2.3 %), the increase in the availability of essential nutrients for grapevines (P_2O_5, 13.8 $mg \cdot kg^{-1}$) and $CaCO_3$ suitable for cultivation (1.9 %). There is no adverse absorption of the major and trace elements in grapevine leaves and, furthermore, there is no increase in the amount of trace elements above reference levels in the region.

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