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RESEARCH ARTICLE

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Assessing the effects of soil liming with dolomitic limestone and sugar foam on soil acidity, leaf nutrient contents, grape yield and must quality in a Mediterranean vineyard

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Abstract

Aluminium toxicity has been recognized as one of the most common causes of reduced grape yields in vineyard acid soils. The main aim of this study was to evaluate the effect of two liming materials, *i.e.* dolomitic lime and sugar foam, on a vineyard cultivated in an acid soil. The effects were studied in two soil layers (0-30 and 30-60 cm), as well as on leaf nutrient contents, must quality properties and grape yield, in an agricultural soil dedicated to *Vitis vinifera* L. cv. 'Mencía' cultivation. Data management and analysis were performed using analysis of variance (ANOVA). As liming material, sugar foam was more efficient than dolomitic limestone because sugar foam promoted the highest decrease in soil acidity properties at the same calcium carbonate equivalent dose. However, potassium contents in vines organs, including leaves and berries, seemed to decrease as a consequence of liming, with a concomitant increase in must total acidity. Soil available phosphorus also decreased as a consequence of liming, especially with sugar foam, though no effects were observed in plants. For these reasons fertilization of this soil with K and P is recommended along with liming. Grape yields in limed soils increased, although non-significantly, by 30%. This research has therefore provided an important opportunity to advance in our understanding of the effects of liming on grape quality and production in acid soils.

Additional key words: acid soil; cultivar 'Mencía'; fruit set; aluminium saturation; total acidity.

Abbreviations used: AlECEC (exchangeable aluminium); C (control); CaECEC (exchangeable calcium); CCE (calcium carbonate equivalent); CI (confidence interval); DL (dolomitic limestone); ECEC (effective cation exchange capacity); ICP-AES (inductively coupled plasma atomic emission spectroscopy); KECEC (exchangeable potassium); MgECEC (exchangeable magnesium); pH_w (pH in water); SOM (soil organic matter); SF (sugar foam).

Authors' contributions: Conceived and designed the experiments and performed the experiments: MAO, MJQ and EGJ. Analyzed the data: MAO, FV, MJQ and JMdeP. Wrote the paper: MAO and FV.

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Introduction

Soil acidity naturally develops because of different factors of soil formation acting alone or in combination: parent materials low in bases, and climates favouring strong leaching. Besides, it can be boosted by various fertilization practices involving nitrogen and manures (Zapata, 2004; Fageria & Baligar, 2008). In addition to low pH, *i.e.*, high H_3O^+ concentration in the soil solution, aluminium (Al) and manganese (Mn) phytotoxicity severely decreases the productivity of crops such as vines on acid soils (Illera *et al.,* 2004), thereby affecting the long-term economic viability of vineyard production and resulting, in some cases, in permanent degradation of the soil as an agricultural resource. Specifically, several studies have dealt with the harmful effects soil acidity has on vines roots. In old vineyards on acid soils, for example, the root system has been observed to abruptly end at the depth where the pH value drops and the Al^{3+} concentration increases significantly (Meyer *et al.*, 1984). This is because the primary target of Al stress in grapevine rootstocks is the actively growing root tip, which is revealed by a severe inhibition of root growth (Cançado *et al.*, 2009). Moreover, Kirchhof *et al.* (1991), in their research developed on *Vitis vinifera* cv. 'Chardonnay', showed how acidic soil conditions, mainly in the subsoil, constrained growth of vine roots. The problems caused by soil acidity on the development of vines can be, however, alleviated by practices aimed at dropping the soil exchangeable aluminium content (AlECEC) below a characteristic critical threshold, as well as for maintaining soil pH above 5.5.

Liming is one of the main methods used by farmers to enhance the fertility of acid soils because: (i) it decreases the contents of exchangeable Al^{3+} by replacement with Ca^{2+} and Mg^{2+}; (ii) it decreases the contents of soluble Al^{3+} by precipitation with the hydroxyl anions generated by carbonate hydrolysis in the soil solution; and (iii) it increases the pH characteristic of acid soils because of such hydrolysis. Through soil acidity neutralization, liming eliminates not only the toxicity of Al^{3+} and H_3O^+, but also on the Mn^{2+} toxicity. Besides, it enhances the availability of Ca^{2+}, Mg^{2+}, P and Mo and, as a consequence, plant nutrition and soil structure (aeration) improve. However, overliming can excessively decrease soil contents of several micronutrients like iron, manganese, zinc, copper and boron, thus leading to various crop deficiencies (Fageria & Baligar, 2008). Wooldridge *et al.* (2010), according to their research on a mixture of cv. Pinot noir and Chardonnay with several vine rootstocks cultivated on acid soils, concluded that liming should be carried out to the point where the vigour of the scion/rootstock combination just ceases to show further benefit.

The effectiveness of liming materials depends on (i) its neutralizing power, which is accounted for by its calcium carbonate equivalent (CCE), and (ii) its fineness (Edmeades & Ridley, 2003; Álvarez *et al.,* 2009). The liming materials used in agriculture are mainly limestone ($CaCO_3$) and marls, and secondarily quicklime (CaO) and slaked lime ($Ca(OH)_2$). Dolomitic limestone and sugar foams are two other materials often used for liming. Dolomitic limestone comprises mainly the mineral dolomite, which is made of a calcium and magnesium double carbonate ($CaMg(CO_3)_2$). Two important characteristics of dolomitic limestone as liming material are: (i) its high neutralizing capacity, featured by CCE of 109 (Tisdale *et al.*, 1993), and (ii) its low dissolution rate, which is approximately 100-fold below that of calcite (Loeppert & Suarez, 1996). Sugar foams are sugar beet-manufacturing residues, which arise from the purification-flocculation of colloid matter in the beet extract by treatment with lime and carbon dioxide (Vidal *et al.,* 2006). This industrial by-product can be used to correct soil acidity and Al phytotoxicity in acid soils because of its high content in active lime. In addition, this liming material contains abundant organic matter and several essential micronutrients (Vidal *et al.,* 1997). Specifically, sugar foams contain about 60% calcium carbonate, 30% water, and 10% inorganic and insoluble organic compounds, mostly beet-plant tissues, in addition to nutrients Se, Zn, and Mo. As a consequence, sugar foams have been considered ideal as agricultural soil-enhancers because through its use, farmers give some of the nutrients separated from the sugarbeet juice back to the soil (Asadi, 2007).

The application of sugar foams is a widespread practice, especially in the last 20 or 30 years, due to the improvements observed in soil properties (Sikora & Azad, 1993). Although extensive research has been carried out on the effects of liming on the properties of acid soils, little is known about the effects of liming on grape quantity and quality of vines cultivated on acid soils. Specifically, the effects of liming on nutrient distribution in grapevine vegetative parts, *e.g.* leaf blades and petioles, grape berries, as well as on crop yield and must quality, are not fully understood yet. Neither the influence of soil liming on Ca, Mg, K and P contents in grape berries has been investigated. Since dolomitic limestone and sugar foams are considered to be able to effectively counteract the symptoms of aluminium toxicity in plants, the specific effects these materials have on plants, in addition to soils, demand further research. Thus, the objective of this investigation was to study for a period of three years the effects on an acidic soil of one single application of two liming materials (dolomitic limestone and sugar foam), on soil properties (acidity, base saturation, etc.), leaf and grape nutrient contents (Ca, Mg, K and P), and finally grape yield and must quality in a vineyard.

Material and methods

Study site

The study site was a commercial vineyard located 556 meters above sea level in the municipality of Cacabelos (León; Spain) with geographic coordinates of 42°36'N latitude and 6°45'W longitude. This area can be considered as representative of vineyards on acid soils under a Mediterranean climate. This type of vineyards occupies over 210,000 ha in Mediterranean Europe (ESD, 2004).

From a climatic point of view, the research area would be classified as Region I (≤ 1,390 Celsius degree-days) based on the system devised by Amerine & Winkler (Jackson, 2014). The mean reference evapotranspiration (FAO Penman-Monteith) and mean rainfall were 922 mm/year and 616 mm/year for the period 2010/11, respectively (SIAR, 2012). The soil under study is an Inceptisol, Suborder Xerept, Great group Haploxerept according to Soil Survey Staff (2010) and Cambisol Dystric according to IUSS Working Group WRB (2006). The soils in the study area are developed on Tertiary sediments from which calcium minerals are almost completely absent (IDEE, 2012).

The research was conducted on *Vitis vinifera* cv. 'Mencía' grafted on a 60-year-old 'Rupestris du Lot' rootstock, which has been classified as highly sensitive to soil acidity (Fráguas, 1999). Planting lines displayed a north-south orientation. The conduction system involved a head trained spur pruned vines, with 4-5 arms per plant. Winter pruning left a thumb-sized arm with two buds. Vineyard had no irrigation system support. No fertilizers or extra amendments other than those used in this research were applied during the study period.

Characterization of the liming materials

The composition of the two liming materials used in this study is shown in Table 1. As expected, the dolomitic limestone exhibited a higher Mg content than the sugar foam, whereas this latter presented a higher organic matter content. Espejo (2001) stated that the high Ca content of the sugar foam is due mainly to the presence of Ca in the form of slaked lime ($Ca(OH)_2$) and, to a lesser extent, as carbonate ($CaCO_3$). The slaked lime progressively reacts with atmospheric CO_2 to produce $CaCO_3$. This carbonation occurs at a rate which depends on the aggregate size, porosity and water content of the sugar foam.

Table 1. Chemical composition of the two liming materials, dolomitic limestone (DL) and sugar foam (SF), expressed on a dry matter basis.

	Liming material	
	DL	**SF**
CaO (g/kg)	311	404
MgO (g/kg)	184	14.5
Na_2O (g/kg)	1.20	0.40
K_2O (g/kg)	3.50	0.90
Al (mg/kg)	9530	2470
Fe (mg/kg)	10500	1420
Mn (mg/kg)	361	121
Cu (mg/kg)	12.0	12.0
Zn (mg/kg)	26.0	32.0
OM[a] (g/kg)	0.0	79.0
CCE[b] (g/kg)	1012	758

Source: Vidal-Bardán & Villa-Bermejo (2012). [a]OM, organic matter; [b]CCE, calcium carbonate equivalent.

Experimental design and liming doses

The experimental design was based on three treatments (control, dolomitic limestone and sugar foam) with three replications each. The whole study plot was therefore split into nine 450 m^2 subplots in which approximately 180 vines were grown each one at 1.5 × 1.7 m spacing in a completely randomized design. The lime requirement was calculated using the formula proposed by Cochrane *et al.* (1980) to achieve 80% base saturation. Therefore, 2720 kg/ha of CCE, which corresponded to 2800 kg/ha of dolomitic lime and 3900 kg/ha of sugar foam were applied. The dolomitic limestone was in a powdery state, whereas the sugar foam consisted of aggregates of variable size, which were manually disaggregated before addition to the soil. The liming materials were uniformly spread onto the entire surface of the treatment subplots, and then incorporated with one-pass tillage down to a depth of 20-30 cm in late November 2008.

Soil, leaf and grape analyses

Before the amendments were added, the soil was sampled and ground to pass a 2-mm mesh sieve. Textural classes according to USDA were determined by the Bouyoucos´s (1962) hydrometer method. Official methods of analysis (MAPA, 1993) were used for the determination of soil organic matter, pH in water (pH_w), electrical conductivity (EC), and the exchangeable contents of Ca, Mg, and K by atomic absorption spectrometry. The exchangeable content of Al was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using 1 M KCl as extractant (Little, 1964). The ECEC was obtained by addition of the exchangeable Ca, Mg, K, and Al contents. CaECEC, MgECEC, KECEC and AlECEC were therefore calculated as the respective quotients: Ca/ECEC, Mg/ECEC, K/ECEC and Al/ECEC, and expressed in %. The available P was determined by visible molecular absorption spectroscopy after extraction with 0.5 M sodium bicarbonate (Olsen *et al.,* 1954).

After liming, the following soil properties were monitored for three years (2009, 2010 and 2011): pH_w, P, CaECEC, MgECEC, KECEC and AlECEC. This monitoring was conducted by sampling the soil in all subplots at 0-30 and 30-60 cm depths, and at the fruit set phenological stage, which occurs in late June in the study area. These depths were chosen because of the depth down to which lime had been incorporated. This was 20-30 cm, and it gave rise to a soil divided into two layers: one directly and another indirectly affected by liming. The soil samples were collected using an auger, sealed in plastic bags, transported to the laboratory and air-dried at room temperature.

The calcium, magnesium, potassium and phosphorus contents in blades and petioles were annually monitored along with the soil properties at the fruit set phenological stage. Specifically, 30 grape basal leaves from opposite bunches were randomly collected per subplot each year in mid-June. They were sealed in plastic bags, and transported to the laboratory. Once in the laboratory the leaves were carefully rinsed with deionized water, and then dried for three days at 70ºC (Bavaresco *et al.,* 2010). Next, they were wet digested with an acid mixture of perchloric, sulphuric and nitric acid at 420ºC for 20 min (Calleja, 1978). The cation contents in the extracts were determined by ICP-AES with quartz torch using a Perkin Elmer Plasma 1000 (Perkin Elmer, Waltham, MA, USA), whereas P content was determined by visible molecular absorption spectroscopy.

The grapes were sampled at harvest every year, specifically on 12th September 2009, 20th September 2010 and 11th September 2011. Those harvested grapes from each subplot were weighed to determine yield. Next, 300 grape berries per subplot were randomly chosen to determine the berry weight parameter, and to analyze must quality. The berry weight parameter was obtained by simply weighing 100 of these berries. The grape must was manually obtained from the 300 berries by gently pressing the grapes, using rubber gloves to avoid sample contamination. In the must thus obtained, the following properties were determined: actual acidity (pH), total soluble solids, total acidity, extractable anthocyanins, and finally, seed maturity. Total soluble solids were measured using a refractometer. Total acidity was determined by titration of the grape must with 0.1 M NaOH to an endpoint of pH 7, and expressed as the equivalent content of tartaric acid in g/L (OIV, 2014). Extractable anthocyanins and seed maturity were determined by the Glories method (Saint-Cricq *et al.*, 1998) and expressed in %. To determine grape nutrient contents, the seeds, skins and flesh from 100 grapes were manually separated and immediately dried at 60ºC to constant weight before wet digestion (Calleja, 1978). Calcium, magnesium, potassium and phosphorus were determined in these extracts by ICP-AES. Calcium, magnesium, potassium and phosphorus in dried grape berries were subsequently assessed as the sum of their contents in skins, seeds and flesh.

Data analyses

Statistical analyses were performed using the R software (R Core Team, 2013). Several analysis of variance (ANOVA) were carried out to study the effect of liming on soil, leaf, grape yield contents, grape must quality properties and grape nutrient contents. In the ANOVAs of the soil chemical properties, the soil depth was also taken into account as a block factor with two levels, *i.e.* shallow soil (0-30 cm), and deep soil (30-60 cm). In all the ANOVAs the year of sampling with three levels (2009, 2010 and 2011) was also included as a block factor. Therefore, a three-way ANOVA (liming, soil depth and sampling year) was used for each one of the soil properties, whereas a two-way ANOVA (liming and sampling year) was used for the leaf, grape yield, grape must quality properties, and grape nutrient contents.

As long as the liming factor presented a significant effect on any of the properties, the variance of the ANOVA between groups, *i.e.* due to the liming factor, was split into two independent (orthogonal) variance contributions (summands) or main effects. These are the effect of just liming, and the effect of the specific material used to lime. Provided the experimental design, these are the only two possible contributions to the variance due to the liming factor. This variance decomposition gives rise to two orthogonal contrasts. In the first contrast, liming is compared against no-liming (C1), *i.e.*, the control is compared against the dolomite and sugar foam treatments lumped together. In the second contrast, the liming materials are compared against each other (C2). The orthogonal contrasts allow measuring the effect sizes in a standardized way and thus, they are more rigorous and statistically efficient than the *post hoc* contrasts used in common practice (Field, 2012).

Before doing the ANOVA the univariate normality hypotheses for every variable were tested using the Kolmogorov-Smirnov test. All soil, leaf (blades and petioles), yield and quality must properties presented univariate normality. Additionally the null hypothesis that the variances of the groups are not different was tested using Levene's tests. According to this test the hypothesis of homoscedasticity could be accepted for every variable at the 95% confidence level.

Results

Soil initial characterization before liming

Table 2 shows the baseline characteristics of the two soil depths before liming. The AlECEC was 37 ± 7% (95% CI) in the 0-30 cm layer, and 42 ± 19% (95% CI) in the 30-60 cm layer. In both depth intervals the exchangeable Al content is over the 20% limit, which is considered the highest Al saturation that most plants can tolerate (Fageria & Baligar, 2008). Additionally, the important exchangeable soil acidity was revealed by the near-one differences between pH_w and pH_{KCl} in both soil layers. Low P, and low exchangeable Ca, K and Mg contents were found too.

Table 2. Baseline soil characteristics before liming.

	Depth (cm)	
	0-30	30-60
Sand (%)	17.5	21.5
Silt (%)	52.2	48.2
Clay (%)	30.3	30.3
Textural class (USDA)	Sandy clay loam	Clay loam
pH$_w$[a]	4.85	4.98
pH$_{KCl}$[b]	4.05	3.96
EC[c] (dS/m)	0.04	0.05
SOM[d] (%)	2.24	1.92
CaECEC[e] (%)	39.5	35.1
MgECEC[e] (%)	16.3	15.4
KECEC[e] (%)	7.60	7.10
AlECEC[e] (%)	36.6	42.1
P[f] (mg/kg)	8.30	7.50

[a]pH$_w$, pH in water; [b]pH$_{KCl}$, pH in 1 M KCl; [c]EC, electrical conductivity; [d]SOM, soil organic matter; [e]CaECEC, MgECEC, KECEC and AlECEC: Ca, Mg, K and Al saturation of the effective cation exchange capacity espectively; [f]P, phosphorus.

Soil properties

The evolution throughout the three years of monitoring of pH$_w$, CaECEC, MgECEC, KECEC and AlECEC and P for the treatment and control subplots, are shown in Figs. S1 and S2 [supplementary]. As can be seen, sugar foam seems to be more efficient than dolomitic lime to decrease soil acidity, especially to reduce AlECEC, and increase CaECEC and pH$_w$ at both study depths. This effect was particularly marked the first year, while differences between sugar foam and dolomite tended to disappear the second year. Interestingly, available P tended to decrease as a consequence of liming, particularly with sugar foam (Fig. 1). Three-way ANOVAs were used to find out if the differences between liming treatments were statistically significant, and furthermore, if they depended on the soil depth and on the year of sampling, and the interactions between both. According to the results of the three-way ANOVAs,

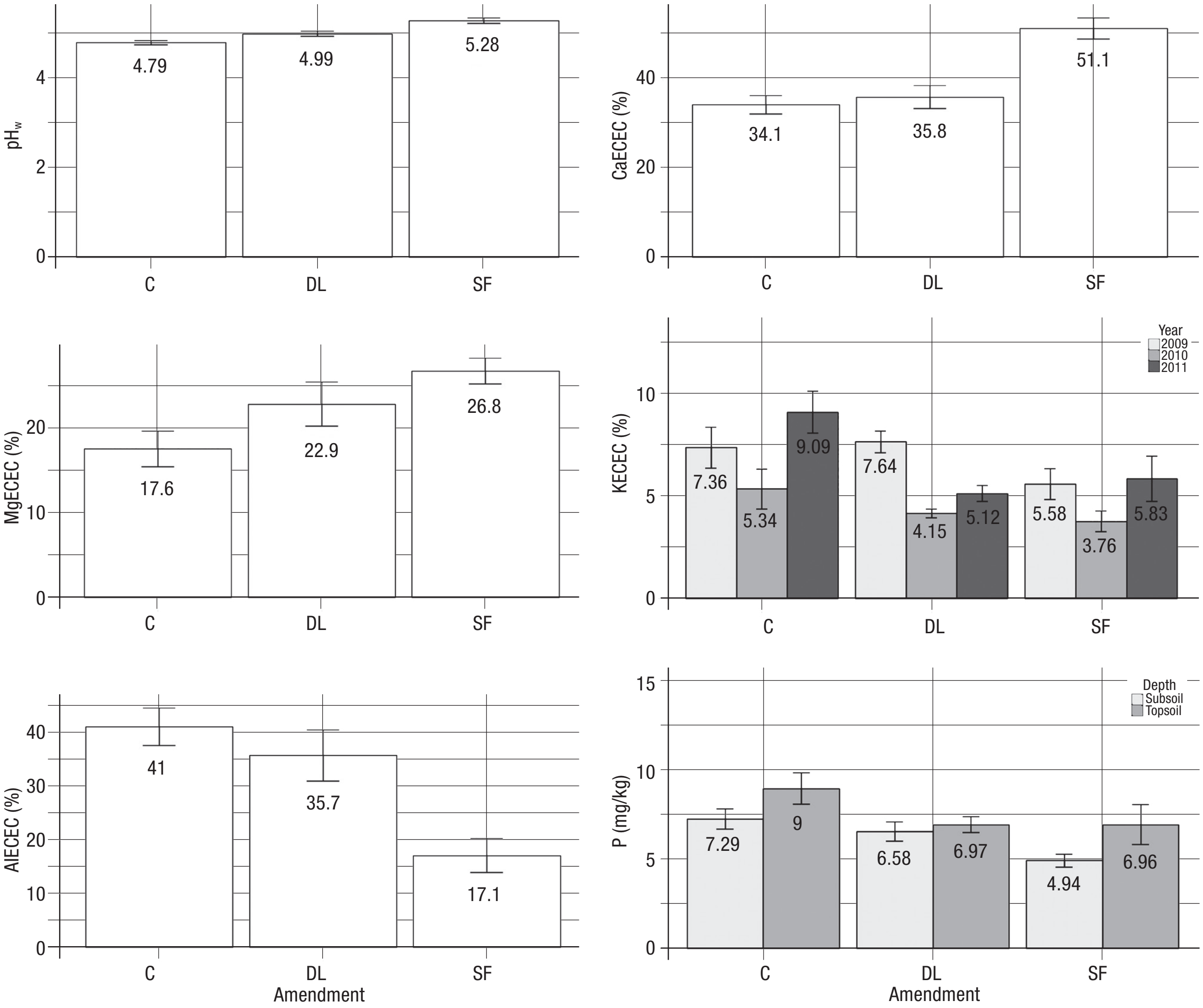

Figure 1. Bar graphs of the soil properties pH$_w$, CaECEC, MgECEC, KECEC, AlECEC and P. Standard errors are shown as ± 1 SE bars. Amendments: C, control; DL, dolomitic limestone; SF, sugar foam.

significant effects of liming on all soil properties were revealed (Table S1 [supplementary]). Besides, the effect of soil depth was revealed as significant just on P levels, whereas the year of sampling was revealed as significant only on exchangeable K. On the contrary, for the other chemical properties the effect of liming does not significantly change either with the soil depth, or with the year of sampling, and neither there are significant interactions between the three factors. Thus, whereas KECEC and P must be studied as, respectively, a function of liming and year of sampling, and a function of liming and soil depth, pH$_w$, CaECEC, MgECEC and AlECEC can be studied as a function of just liming (Fig. 1).

Therefore, one-way ANOVAs were carried out for each soil property (Table 3), and again significant differences of pH$_w$, CaECEC, MgECEC and AlECEC were observed between treatments. Specifically, pH$_w$, CaECEC and MgECEC increased while AlECEC decreased in soils in which liming materials were used. However, in order to find out if differences in the soil properties between treatments arose as a consequence of i) just liming (C1), or ii) liming with sugar foam or dolomitic limestone (C2), or iii) both (C1 + C2), the variance between treatments obtained from the one-way ANOVAs was decomposed according to both planned contrasts (C1 and C2). The first contrast (C1) revealed that just liming significantly increased pH$_w$, CaECEC and MgECEC, whereas significantly decreased KECEC and AlECEC. The second contrast (C2) revealed that sugar foam significantly increased pH$_w$, KECEC (in 2011) and CaECEC, whereas significantly decreased P, in the subsoil layer, and AlECEC more than dolomitic limestone (Table 3). After three years the effects of liming with both materials, and particularly with sugar foam, on all six soil properties were still remarkable (Table 4).

Table 4. Differences between the averages of the six monitored soil properties in dolomite-limed plots and controls (DL-C) and sugar foam-limed plots and controls (SF-C) at the end of the experiment and at the two soil depths. Standard errors (SE) of the difference are shown as ± SE.

Parameter	Depth (cm)	DL-C	SF-C
pH$_w$	0-30	0.12 ± 0.30	0.24 ± 0.24
	30-60	0.19 ± 0.37	0.52 ± 0.33
CaECEC (%)	0-30	6.54 ± 15.7	19.9 ± 14.9
	30-60	–0.67 ± 15.4	17.0 ± 12.9
MgECEC (%)	0-30	4.42 ± 13.7	2.27 ± 10.1
	30-60	1.86 ± 14.3	9.06 ± 9.02
KECEC (%)	0-30	–3.50 ± 1.86	–2.68 ± 3.10
	30-60	–4.43 ± 2.48	–3.83 ± 3.00
AlECEC (%)	0-30	–7.46 ± 27.9	–19.5 ± 22.8
	30-60	3.25 ± 27.6	–22.3 ± 18.2
P (mg/kg)	0-30	–3.14 ± 1.16	–0.64 ± 1.88
	30-60	–0.33 ± 1.52	–2.13 ± 1.20

Table 3. Effects and effect sizes of liming against control (C1), and liming with sugar foam against liming with dolomitic limestone (C2), on soil properties at the fruit set stage.

Soil property	Factor	One-way ANOVA		Contrast	Mean$_d$[c]	t-ratio	*p*-value	r[d]
		F-value	*p*-value					
pH$_w$[a]	LM	18.5	***	C1	0.34	4.90	***	0.57
				C2	0.29	3.61	***	0.45
P (mg/kg)	LM on 0-30 cm	1.84	0.18	C1	–2.03	–1.66	0.11	–
				C2	–0.01	–1.67	0.11	–
	LM on 30-60 cm	5.74	**	C1	–1.53	–1.00	0.33	–
				C2	–1.64	–3.30	**	0.56
CaECEC[b] (%)	LM	16.2	***	C1	9.30	3.26	**	0.42
				C2	15.4	4.67	***	0.55
MgECEC[b] (%)	LM	4.73	*	C1	7.25	2.80	**	0.37
				C2	3.84	1.28	0.21	–
KECEC[b] (%)	LM on 2009	2.03	0.17	C1	0.28	0.25	0.81	–
				C2	–1.79	–1.61	0.13	–
	LM on 2010	1.63	0.23	C1	–1.19	–1.30	0.21	–
				C2	–1.58	–1.73	0.10	–
	LM on 2011	5.56	*	C1	–3.97	–3.13	**	0.63
				C2	–3.25	–2.56	*	0.55
AlECEC[b] (%)	LM	10.6	***	C1	–14.6	–3.09	**	0.40
				C2	–18.6	–3.41	**	0.43

*significant at the $p<0.05$ level; **significant at the $p<0.01$ level; ***significant at the $p<0.001$ level. LM, liming material factor; [a]pH$_w$, pH in water; [b]CaECEC, MgECEC, KECEC and AlECEC: Ca, Mg, K and Al saturation of the effective cation exchange capacity respectively; [c]Mean$_d$ (mean differences between control and amendments for contrast 1, and between sugar foam and dolomite for contrast 2); [d]r (effect size).

Leaf nutrient contents

Means and standard errors of Ca, Mg, K and P content in blades and petioles for the dolomitic limestone and sugar foam treatment, and control subplots are shown in Fig. 2. The shaded areas in Fig. 2 illustrate the concentration ranges that are optimal at fruit set for petioles (Ca (0.6 – 1.4%), Mg (0.3 – 0.8%), K (1.0 – 2.9%) and P (0.1 – 0.6%)) according to Wooldridge *et al*. (2010), and blades (Ca (1.4 – 2.6%), Mg (0.2 – 0.4%), K (0.8 – 1.4%) and P (0.1 – 0.3%)) according to Fregoni (2005).

According to the ANOVAs there were no significant effects (p>0.05) of liming on any of the leaf

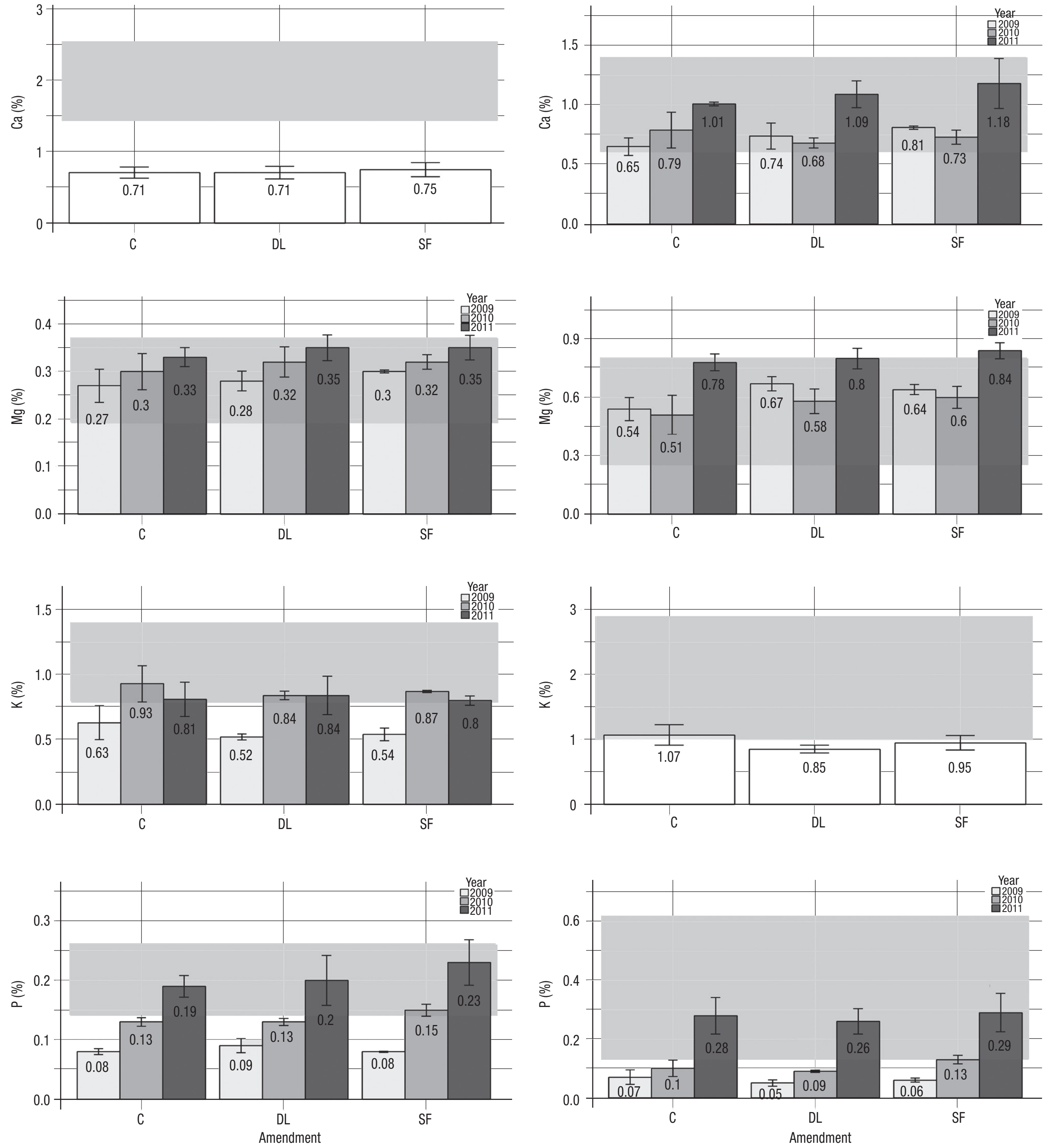

Figure 2. Bar graphs of blade (left-hand column) and petiole (right-hand column) element composition at fruit set. Standard errors are shown as ± 1 SE bars. The shaded areas in the graphs illustrate the concentration ranges that are optimal for adequate vine growth at fruit set according to Fregoni (2005) for blades and Wooldridge *et al*. (2010a) for petioles. C: control; DL: dolomitic limestone; SF: sugar foam.

nutrient contents in both blades and petioles. Interestingly, there was a significant effect ($p<0.05$) of year of sampling on Mg, K and P in blades, as well as on Ca, Mg and P in petioles, whereas the interaction between liming and sampling year was not significant ($p>0.05$) on any of the leaf nutrient contents. Correlation coefficients (not shown) between magnesium, calcium, potassium and phosphorus in leaf and in soil were very low.

Yield, must quality and grape nutrient contents

There were no significant effects ($p>0.05$) of liming on berry weight, grape yield, total soluble solids, pH and extractable anthocyanins. On the contrary, there were significant effects of liming on total acidity just in 2011, and seed maturity just in 2009 and 2010 (Table 5). Interestingly, there was a significant effect ($p<0.05$) of year of sampling on berry weight, total acidity, extractable anthocyanins and seed maturity (Table S2 [supplementary]). It is also interesting the absence of significant interactions between liming and sampling year in all parameters except seed maturity. Therefore, means along with standard errors are shown in Fig. 3 for grape yield, total soluble solids and pH by liming material, while the same statistics are shown for berry weight, total acidity, extractable anthocyanins and seed maturity by both liming material and year.

According to the ANOVA, liming had no significant effects ($p>0.05$) on any of the nutrient contents. Interestingly, there was a significant effect ($p<0.05$) of year of sampling on K and P contents in grapes. Additionally, the effect of the sampling year on the grape nutrient contents did not change with liming. This was revealed by the non-significant interaction ($p>0.05$) between liming and sampling year. Thus, mean and standard errors of Ca and Mg content in grapes by liming material, and the same statistics of K and P contents in grapes by liming material and year are shown in Fig. 4.

Discussion

In the Haploxerept acid soil studied in this work, liming was effective in decreasing soil acidity, as well as in increasing calcium and magnesium exchangeable contents. Besides, liming with sugar foam was more effective and its effects developed earlier than liming with dolomitic limestone. These results are similar to those obtained by García Navarro *et al.* (2009) on other dryland crops, and other soils (Anthrosols and Luvisols). Interestingly, although liming materials were incorporated with one-pass tillage down to a depth of 20-30 cm, no significant differences in properties were found between the arable and the underlying soil layers (0-30 and 30-60 cm), which indicates significant redistribution of calcium and magnesium within the soil regardless of the liming material used. This contrasts with the results of González *et al.* (2005) in "Raña" soils, in which dolomitic limestone caused different migration of Ca and Mg below the arable layer compared with sugar

Table 5. Effects and effect sizes of liming against control (C1), and liming with sugar foam against liming with dolomitic limestone (C2), on total acidity (TA, g tartaric acid/L) and seed maturity (SM, %) at harvest time.

Enological parameter	Factor	One-way ANOVA		Contrast	Mean_d	t-ratio	*p*-value	r
		F-value	*p*-value					
TA	LM on 2009	0.38	0.70	C1	–0.15	–0.34	0.74	–
				C2	0.23	0.52	0.62	–
	LM on 2010	1.43	0.31	C1	0.05	0.32	0.76	–
				C2	0.25	1.60	0.16	–
	LM on 2011	8.82	*	C1	0.50	1.25	0.26	–
				C2	1.64	4.10	**	0.86
SM	LM on 2009	6.11	*	C1	6.03	2.94	*	0.77
				C2	–0.33	–0.16	0.88	–
	LM on 2010	9.63	*	C1	6.97	4.35	**	0.87
				C2	4.33	2.70	*	0.74
	LM on 2011	2.12	0.21	C1	–2.53	–1.24	0.26	–
				C2	–4.20	–2.05	0.09	–

*significant at the $p<0.05$ level; **significant at the $p<0.01$ level. LM, liming material factor.

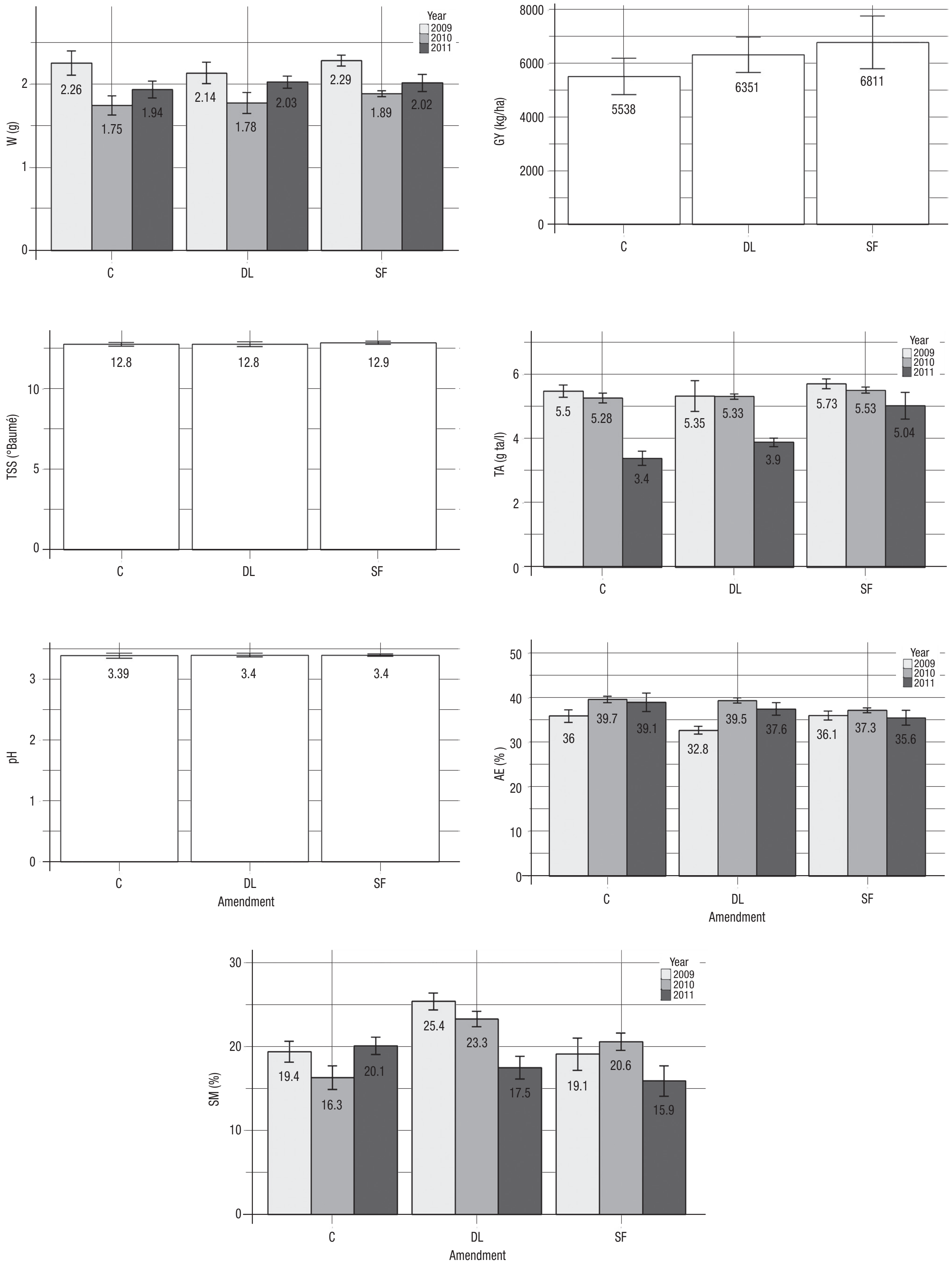

Figure 3. Bar graphs of berry weight (W), grape yield (GY), total soluble solids (TSS), total acidity (TA), pH, anthocyanin extractability (AE) and seed maturity (SM) (2009-2011). Standard errors are shown as ± 1 SE bars. C: control; DL: dolomitic limestone; SF: sugar foam.

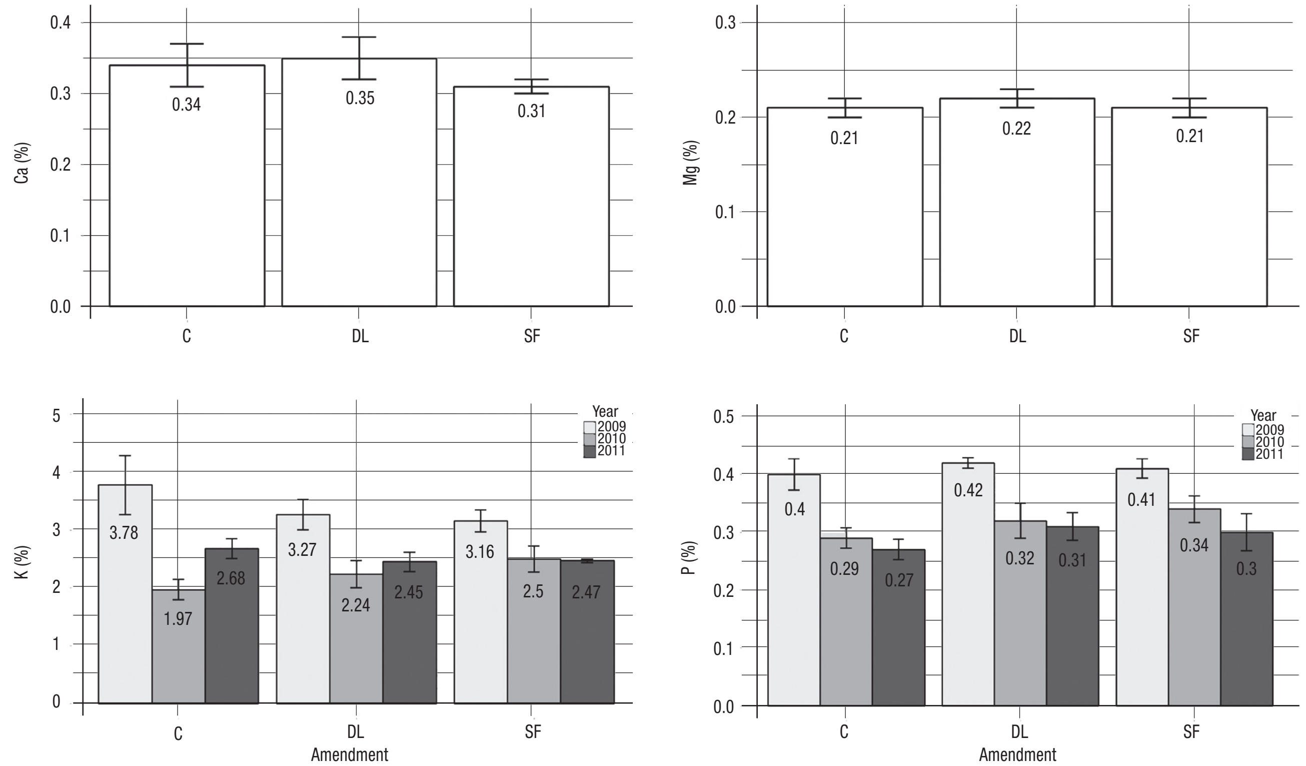

Figure 4. Bar graphs of Ca, Mg, K and P contents in grape berries. Standard errors are shown as ± 1 SE bars. C: control; DL: dolomitic limestone; SF: sugar foam.

foam. The remarkable higher efficiency and faster effect of sugar foam over dolomitic limestone could be explained on basis the higher solubility of $Ca(OH)_2$ over $CaMg(CO_3)_2$, which is roughly three orders of magnitude higher. In this regard, there are similarities between the effect of sugar foam in the levels of CaECEC and AlECEC in this study and those described in a previous work by Olego *et al*. (2014c).

The highest soil exchangeable Mg content in soils limed with sugar foam compared to dolomitic limestone could be explained also on a solubility basis: the form in which magnesium is present in sugar foam is $Mg(OH)_2$, which is more soluble than $CaMg(CO_3)_2$. Besides, magnesium fertilizers can be grouped into four classes according to their dissolution rates: $MgSO_4 > MgO \approx Mg(OH)_2 >$ slag lime ≈ dolomitic limestone ≈ magnesite > basalt (Augustin *et al.*, 1997), which additionally contributes to explain why sugar foam is more effective than dolomitic limestone as liming material. Interestingly, under laboratory conditions soils amended with dolomitic limestone have shown significantly higher exchangeable Mg contents than those treated with sugar foam (Vidal *et al.*, 2006). This points to the importance of having information from field trials or, alternatively, from validated models, before any management decision is reached. Information from field trials or from validated models, is preferred because this way the variability and effects of many factors absent under laboratory practice such as crop management, weather, and other environmental conditions are taken into account.

Exchangeable K contents decreased, though not significantly, after liming. However, the difference was statistically significant in the third year. This barely significant downward trend of exchangeable K content in limed subplots approximately matched the non-significant drop trend of K on blades and petioles and furthermore, in berries. Therefore, the vines have been able to buffer the K contents in plant tissues, although not completely, which could have had consequences on the must total acidity.

In general, liming did not cause differences in must quality properties. However, it is interesting to note that must total acidity was higher in limed subplots, specifically the last year of monitoring, and this effect was more pronounced with sugar foam than with dolomite limestone. When potassium grape content increases, must total acidity decreases and must pH increases (Conde *et al.*, 2007). In our trials this effect could have been driven by liming because of the increase of soil Ca and Mg exchangeable contents, which along with the antagonistic interaction of Ca and Mg with K could have decreased the K plant uptake (Fageria, 1983; Dibb & Thompson, 1985), as discerned on basis the leaf K contents. Although the effect did not extend to the extractable anthocyanins and seed maturity, addition of K fertilizers along with liming is recommended, given the importance of K berry contents on vinification.

One of the primary reasons for liming acid soils is to increase soil P availability to plants (Sánchez & Uheara, 1980). Moreover, in acid soils containing exchangeable aluminium on alumino-silicate or organic exchange sites, P reaction with exchangeable aluminium controls the P solubility (Traina *et al.,* 1986), and furthermore, liming materials, and specifically sugar foams, contain significant amounts of P (between 0.8 and 2.25% the latter). Notwithstanding this, and in contrast to earlier findings (García Navarro *et al.,* 2009) which showed an increase in available soil P as a consequence of liming with sugar foams, in this study soil P availability significantly dropped as a consequence of liming, and significantly more with sugar foam than with dolomite limestone, and more in the subsoil layer. However, in spite of this effect on soil, P levels in plant organs, leaves and berries, did not present significant differences between treatments, which points to the strong P buffer ability of the plant. Furthermore, the decrease in available P during the first two years in the sugar foam limed plots, and the subsequent increase in the third year points to a change in P speciation. Since moderate increments of pH by liming of acid soils not only raise P solubility but also promote the transfer of P from $AlPO_4$ minerals, *e.g.* variscite, to Ca phosphates, these differences suggest that these contradictory results may be in part due to that Olsen's extractant is perhaps more effective to release P from $AlPO_4$ minerals than from Ca phosphates in the soil studied in this work.

Though statistically non-significant, an increasing trend in grape yields could be observed in limed subplots (Figure 3), which could have economic effects. Specifically, liming with either sugar foam or dolomite limestone increased grape yields by 13.3% in 2009, 18.7% in 2010 and 27.3% in 2011. This trend can be attributed to higher base saturations in the limed subplots, which in turn bring about more favourable AlECEC/CaECEC and AlECEC/MgECEC interactions (Marschner, 2012). The increase sequence in yield data (C < DL < SF) is consistent with those obtained for CaECEC and MgECEC data (C < DL < SF), as well as to the one obtained for AlECEC data (C > DL > SF). Contrary to this, Wooldridge *et al.* (2010) observed that grape yield decreased with increasing lime application rate when trying different lime rates combined with double superphosphate.

Summing all this up, liming was able to counteract soil acidity while increasing soil exchangeable calcium and magnesium in the acid Haploxerept cultivated with *Vitis vinifera* cv. 'Mencía' which was studied in this work. Besides, sugar foam was more efficient than dolomitic limestone, which may be explained on basis the higher solubility and rate of solubilization of calcium and magnesium minerals in the sugar foam. However, liming tended to decrease the vines K contents, with eventual unfavorable effects on vinification because of changes on must properties, specifically on total acidity. Soil available P contents also dropped as a consequence of liming, specifically with sugar foam, though this effect did not show up in vines P contents, and furthermore it vanished with time. Interestingly, liming seemed to have a favorable effect on grape yields. May be more significant effects would have been revealed using higher liming doses, and also extending the monitoring span to more years. This is interesting overall in the case of dolomite limestone, whose lower efficiency might be partly offset by a greater durability. Addition of K and P fertilizers is also recommended along with lime materials in order to make up for the lower availability of both nutrients, and in order to try to boost yields.

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