Influence of soil pH correction and potassium saturation on quality and stability of Brazilian tropical wines produced in the São Francisco Valley

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Abstract. This study evaluated the influence of soil pH correction and potassium saturation on the quality of Brazilian tropical red wines 'Syrah' from São Francisco Valley. Soil pH correction and potassium saturation were established by applying elemental sulfur, calcium sulphate or potassium chloride to the soil. The experiment followed a 2x3 factorial with two levels of soil exchange complex saturation with base(V) and three percentage of exchangeable potassium in the soil(PKT). The treatments were T1= V 86% and PKT 2.5%; T2 = V 86% and PKT 4.6% (control); T3 = V 86% and PKT 10%; T4 = V 50% and PKT 2.5%; T5 = V 50% and PKT 4.6%, T6 = V 50% and PKT 10%. The results show that high soil PKT value (10%) reduced must potassium content. Lower soil exchange complex saturation with base (V=50%) with median percentage of exchangeable potassium in the soil (PKT=4.6%) resulted in higher total polyphenols content and organic acid degradation in the berry. The V=86% plus PKT 4.6% and the V=50% plus PKT=4.6% resulted in wines with higher amount of precipitates and highest pH value. The results suggest that these soil management conditions will can promote a great effect on wine quality

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1 Introduction

The São Francisco Valley is located in the Northeast of Brazil and represents one of the most distinct winemaking regions in the country. This region is characterized by a semiarid tropical climate with an average annual temperature of 26.5°C and 3,000 sunshine hours per year. These environmental conditions allow grapevine growth and development throughout the year, enabling to schedule up to three grape harvests per year, depending on the genotype and market demand [7,10]. However, red wines produced in the region have been primarily intended for quick consumption in the first two years after bottling due to its chemical instability that is evidenced by color changes from red-ruby to brown.

Wine instability is believed to be the result of high potassium concentrations in the increasing grape potassium concentration and eventually enhancing wine pH and reducing titratable acidity. Grape pH is more sensitive to changes in potassium concentration than to changes in the main organic acids such as tartaric and malic acid. In 10% increase in potassium concentration can enhance pH by 0.1 unit [3,4]. In addition, grapes grown in hot climates, such as the São Francisco Valley, usually have higher pH due to higher acid degradation by the increased respiratory activity. In the wine, potassium can also precipitate with tartaric acid producing potassium bitartrate (KHT), which is precipitates more at pH values higher than 3.7. These precipitates form crystals that accumulate at the bottom of the wine bottles. The amount of KHT precipitate is highly dependent on the amount of potassium, tartaric acid, pH, alcohol and reducing sugar content, and wine temperature and usually increases with wine aging [15]. According to [11] changes in the vineyard soil chemistry, selection of appropriated rootstock, irrigation strategies and canopy management are agronomic procedures that can help reducing potassium accumulation in the soil and translocation to the berries. However, the use of such practices should be extensively studied in order to avoid potassium deficiency or excess. High potassium in the wine can result in high KHT precipitate, whereas low potassium can limit wine alcoholic fermentation [6]. Although pH values can be adjusted during fermentation, fine tuning potassium accumulation in the fruit can be more efficient due to simplification and reduction of the winemaking costs [11].

The vineyard soil chemistry with high sodium content can be managed with the addition of elemental sulfur and calcium sulfate, which have been recommended to recover sodic soils [5]. In the soil, K⁺ is replaced by H⁺ released from sulfur oxidation or by Ca²⁺ released from the calcium sulfate. In both cases, potassium becomes water soluble in the soil solution and is eventually leached with SO₄-2 [13]. It is important to avoid calcium excess in the soil because it can also precipitate with tartaric acid producing calcium tartrate that can also reduce wine stability [15].

The objective of this study was to evaluate the influence of soil pH correction and potassium saturation on the quality of Brazilian tropical red wines produced from 'Syrah' grapes grown in the São Francisco Valley.

2 Material and methods

Soil pH correction and potassium saturation were established by applying elemental sulfur, calcium sulphate or potassium chloride to the soil. After accomplishing greenhouse assays and soil chemical analysis, the experiment was established on August 2012 in a commercial 'Syrah' vineyard (09°16'S; 40°51'O, 444 m, Casa Nova, BA, Brazil). The plants were grafted on 'IAC-766' (106-8 x Vitis caribeae) rootstck. The vineyard was conducted in espalier system and the plants were irrigated by drip irrigation. The soil of the experimental areas is classified as a Red-Yellow Latosol.

The experiment followed a 2 x 3 factorial with two levels of soil exchange complex saturation with base (V) and three percentage of exchangeable potassium in the soil (PKT). There was also a control treatment that followed the standard soil conditions of the commercial vineyard. The treatments were T1= V 86% and PKT 2.5%; T2 = V 86% and PKT 4.6% (control); T3 = V 86% and PKT 10%; T4 = V 50% and PKT 2.5%; T5 = V 50% and PKT 4.6 %; T6 = V 50% and PKT 10%. The experimental design was randomized blocks with four blocks per treatment. Two plant rows were used as buffers between blocks. Each block was composed by six plants.

Grapes were harvested in June, 2013 and vinified in triplicate by the traditional method in the Enology Laboratory at Embrapa Tropical Semi-arid, Petrolina, PE, Brazil. The winemaking process was accomplished in glass bottles of 20L, with alcoholic and malolactic fermentations, conducted at 25° and 18°C, respectively. After stabilization with Stabigum® (Amazon Group), the wines were bottled and

analyzed after 30 days. Plant, fruit, and wine were analyzed as described below.

2.1 Plant nutrient analysis

Plant potassium (K⁺), calcium (Ca²⁺), magnesium (Mg²⁺) and sodium (Na⁺) concentrations were analyzed in petioles of two leaves opposite to the grape bunch from the base of the branch at end of the flowering period. Two petioles were collected per plant on each block.

2.2 Plant yield and vigor

Two plants per block were evaluated for wholeplant shoot and leaf weight. The Ravaz index was determined by the fruit weight/shoot weight ratio per plant.

2.3 Grape and must quality

At harvest, five grape bunches per block were used for the following fruit quality analysis: bunch and berry (n=100) fresh weight; berry skin color (CIE L*a*b*); soluble solids; titratable acidity; polyphenolic compouds [2]; tartaric acid quantified by High-Performance Liquid Chromatography – HPLC (LIMA et al., 2014); as well as K⁺, Ca²⁺, Mg²⁺ and Na⁺ concentrations quantified by Atomic Absorption Spectrometry - AAS.

2.4 Wine quality

Wine samples were analyzed for pH, titratable and volatile acidity, alcohol content, density, dry extract [2], color intensity [12], total monomeric anthocyanins [8], total phenolic content [14], and tartaric acid by HPLC [9].

2.5. Data analysis

Data were subjected to the analysis of variance (ANOVA) using the Statistical Analysis System (SAS®). Mean values were compared using Tukey's test ($p \le 0.05$).

3. Results and discussion

The petiole K⁺, Ca²⁺, Mg²⁺ and Na⁺ concentrations in response to each treatment are presented on Table 1. Treatments had no effect on petioles K⁺, Ca²⁺, Mg²⁺ concentrations. However, the treatment with V 50% and PKT 10% (T6) showed the lowest and the treatments with V 86% and PKT 2.5% (T1) and V 86% and PKT 10% (T3) had the highest Na⁺ in leaf petioles (Table 1).

Table 1. Nutrient concentration in grapevine leaf petioles in response to different soil exchange complex saturation with base (V) and percentage of exchangeable potassium in the soil (PKT). Nutrient analyses was accomplished at end of the flowering period.

Treatments ^{1,2}	K (g kg- ¹)	Ca (a tra 1)	Mg	Na (ma ka l)
	(g kg)	(g kg-1)	(g kg- ¹)	(mg kg- ¹)
T1	20.97 A	17.45 A	3.36 A	550.57 A
T2	19.07 A	19.55 A	3.13 A	515.30 AB
T3	22.11 A	18.34 A	3.00 A	555.61 A
T4	20.21 A	18.65 A	2.98 A	517.82 AB
T5	22.23 A	18.04 A	3.08 A	537.98 AB
T6	19.07 A	19.20 A	3.31 A	492.63 B

 1 T1= V 86% and PKT 2.5%; T2 = V 86% and PKT 4.6% (control); T3 = V 86% and PKT 10%; T4 = V 50% and PKT 2.5%; T5 = V 50% and PKT 4.6 %; T6 = V 50% and PKT 10%. 2 In the same column means showing common letter are not significantly different (p \leq 0.05) according to Tukey's test.

The combinations between different V and PKT had no effect on plant yield and vigor (Table 2). The results obtained in all treatments show that plant yield was very low, which was possibly due to the reduced plant vigor determined by the Ravaz index that ranged from 1.20 to 1.78.

Table 2. Plant yield, shoot and leaf weight, and Ravaz index (vigor) of grapevines in response to different soil exchange complex saturation with base (V) and percentage of exchangeable potassium in the soil (PKT). Evaluations were accomplished at harvest.

Treatments ^{1,2}	Yield (kg plant ¹)	Shoot (g plant ⁻¹)	Leaf (g plant ¹)	Ravaz Index
T1	0.721 A	776 A	718 A	1.23 A
T2	0.630 A	722 A	618 A	1.20 A
T3	0.881 A	644 A	532 A	1.68 A
T4	0.927 A	687 A	553 A	2.13 A
T5	1.026 A	704 A	630 A	1.78 A
T 6	1.001 A	782 A	601 A	1.73 A
Means	0.87	719	870	1.62
CV (%)	24.65	35.89	36.12	36.06

 1 T1= V 86% and PKT 2.5%; T2 = V 86% and PKT 4.6% (control); T3 = V 86% and PKT 10%; T4 = V 50% and PKT 2.5%; T5 = V 50% and PKT 4.6%; T6 = V 50% and PKT 10%. 2 In the same column means showing common letter are not significantly different (p \leq 0.05) according to Tukey's test.

The data obtained show that fruit quality parameters such as bunch and berry fresh weight, and berry skin color were not affected by the treatments (Table Combinations between low V (50%) and high PKT (10%) resulted in lower organic acids content (Table 4). However, the tartaric acid content was lower in grapes grown with V=50% and PKT=4.6% (Table 4). The total polyphenolic compouds were also lower in grapes grown with intermediate PKT levels (T2 - control). The soluble solids content was not affected by the treatments at harvest (Table 4).

Table 3. Bunch and berry weight, and skin color L* a* b*) of grapes grown at different soil exchange complex saturation with base (V) and percentage of exchangeable potassium in the soil (PKT). Evaluations were accomplished at harvest.

Treatments ^{1,2}	Bunch Berry		Skin color			
	(g)	(g)	L	a ^{ak}	b [*]	
T1	133.92 A	1.55 A	30.65 A	6.27 A	6.30 A	
T2	118.81 A	1.68 A	31.14 A	6.36 A	5.94 A	
T3	118.67 A	1.70 A	30.84 A	6.02 A	6.46 A	
T4	168.28 A	1.66 A	31.50 A	5.76 A	6.04 A	
T5	141.44 A	1.72 A	31.11 A	6.09 A	5.98 A	
T 6	133.85 A	1.69 A	30.92 A	6.86 A	5.93 A	

 $^1\text{T1}= \text{V}$ 86% and PKT 2.5%; T2 = V 86% and PKT 4.6% (control); T3 = V 86% and PKT 10%; T4 = V 50% and PKT 2.5%; T5 = V 50% and PKT 4.6 %; T6 = V 50% and PKT 10%. 2 In the same column means showing common letter are not significantly different (p \leq 0.05) according to Tukey's test.

Table 4. Tartaric acid (TART AC), titratable acidity (TA), soluble solids (SS), and phenolic content (PC) in grapes grown at different soil exchange complex saturation with base (V) and percentage of exchangeable potassium in the soil (PKT). Evaluations were accomplished at harvest.

Treatments ^{1,2}	TART AC (g kg ⁻¹)	TA (g 100g-1)	SS (°Brix)	PC (mg 100g ⁻¹)
T1	1.86A	0.57 AB	24.7 A	331.72 A
T2	1.61A	0.61 AB	23.4 A	299.56 B
T3	1.28BC	$0.62~\mathrm{AB}$	25.1 A	339.62 A
T4	1.60A	0.63 AB	24.1 A	345.66 A
T 5	1.13 C	0.69 A	24.8 A	328.43 A
T6	1.57AB	0.52 B	24.5 A	333.90 A

 1 T1= V 86% and PKT 2.5%; T2 = V 86% and PKT 4.6% (control); T3 = V 86% and PKT 10%; T4 = V 50% and PKT 2.5%; T5 = V 50% and PKT 4.6 %; T6 = V 50% and PKT 10%. 2 In the same column means showing common letter are not significantly different (p \leq 0.05) according to Tukey's test.

The nutrient concentration analysis in grape berries revealed that K+ concentration was reduced in fruit grown at V=86% and PKT=10% or at V=50% and PKT=10% (Table 5). Calcium and Na+ concentrations in the berries were not affected by the treatments (Table 5). The highest Mg²⁺ and K+ concentrations were observed in grapes grown at V=86% and PKT=2.5% (Table 5). The results suggest that high soil PKT value (10%) reduced grape and consequently must potassium content, because treatments with PKT=10% (T3 and T6) resulted in the lowest fruit K concentrations (Table 5).

Table 5. Nutrient concentration in grapes grown at different soil exchange complex saturation with base (V) and percentage of exchangeable potassium in the soil (PKT). Evaluations were accomplished at harvest.

Treatments ^{1,2}	K (g kg- ¹)	Ca (g kg- ¹)	Mg (g kg- ¹)	Na (mg kg- ¹)
T1	232.50 A	254.00 A	135.00 A	38.00 A
T2	195.00 AB	221.00 A	88.50 B	30.00 A
T3	182.50 B	267.00 A	88.50 B	26.50 A
T4	197.00 AB	213.00 A	75.00 B	30.00 A
T 5	200.50 AB	201.00 A	77.50 B	30.50 A
T 6	179.00 B	234.00 A	$76.00 \; \mathrm{B}$	27.00 A

 1 T1= V 86% and PKT 2.5%; T2 = V 86% and PKT 4.6% (control); T3 = V 86% and PKT 10%; T4 = V 50% and PKT 2.5%; T5 = V 50% and PKT 4.6 %; T6 = V 50% and PKT 10%. 2 In the same column means showing common letter are not significantly different (p ≤ 0.05) according to Tukey's test.

The Table 6 shows the physic-chemical composition of the wines obtained from the grape grown at different soil exchange complex saturation with base (V) and percentage of exchangeable potassium in the soil (PKT) treatments. Even as the soluble solids of the grapes at harvest did not differed among the treatments (Table 4), the wine's alcoholic content and density were not affected by the treatments (Table 5). Also were not affected by V and PKT the contents of anthocyanins and titratable acidity (Table 5). However, the pH values and tartaric acid content differed among the wines. The pH was highest in the wine of the treatment T5 (V 50% and PKT 4.6 %). This wine was winemaking with the grapes harvested with the lowest contents of tartaric acid according to Table 4. The pH of the wine from the treatment T5 did not differed significantly (p≤0.05) of the wines from the treatments control T2 (V 86% and PKT 4.6%) and T6 (V 50% and PKT 10%). In fact, the Table 4 also showed that combinations between low V (50%)

and high PKT (10%) resulted in lower organic acids content in grapes at harvest. In contrast, the wines of the treatments T5 and T6 presented the highest total phenolic compounds content. But the content of tartaric acid was highest in the wine obtained from grapes grown at high V (86%) and lowest PKT (2.5%) and differed significantly of all other wines.

Table 6. Physic-chemical composition of the wines winemaking with the grapes grown at different soil exchange complex saturation with base (V) and percentage of exchangeable potassium in the soil (PKT) treatments. Density (DEN), pH, titratable acidity in g L-1 (TA), phenolic compounds content in mg L-1 (PC), total monomeric anthocyanins in mg L-1 (ANT), color intensity (CI), volatile acidity in in g L-1 (VA), dry extract in in g L-1 (EXT), alcohol content in % v/v (ALC), and tartaric acid in mg L-1 (TART AC).

soil to the region of the São Francisco Valley it is necessary to study more crops and the wine stability.

Acknowledgements

The authors are grateful to the Miolo Wine Group.

Treatments ^{1,2}	T1	T2	T3	T4	T5	T 6
DEN	0.9918 A	0.9916 A	0.9916 A	0.9918 A	0.9913 A	0.9917 A
pH	3.44 B	$3.49~\mathrm{AB}$	3.19 C	3.14 C	3.70 A	$3.62~\mathrm{AB}$
TA	5.93 A	6.25 A	6.55 A	6.43 A	5.78 A	5.98 A
\mathbf{PC}	$2001.16\mathrm{BC}$	2137.34 AB	2047.61 ABC	1942.04 C	2199.63 A	2179.57 A
ANT	430.39 A	443.08 A	478.14 A	476.06 A	489.28 A	475.64 A
CI	8.84 B	11.15 A	10.88 A	11.30 A	10.80 A	11.86 A
VA	0.67 A	0.059 C	0.42 B	0.40 B	0.48 B	0.45 B
EXT	$22.87~\mathrm{AB}$	21.50 AB	23.77 A	23.50 A	$20.10~\mathrm{B}$	23.33 AB
ALC	12.77 A	12.75 A	13.51 A	13.07 A	12.51 A	14.28 A
TART AC.	742.00 A	378.30 B	201.00 B	283.20 B	417.90 B	168.70 B

 1 T1= V 86% and PKT 2.5%; T2 = V 86% and PKT 4.6% (control); T3 = V 86% and PKT 10%; T4 = V 50% and PKT 2.5%; T5 = V 50% and PKT 4.6%; T6 = V 50% and PKT 10%. 2 In the same line means showing common letter are not significantly different (p \leq 0.05) according to Tukey's test.

After a month of bottling, the V=86% plus PKT 4.6% treatment (T2) and the V=50% plus PKT=4.6% treatment (T5) resulted in wines with higher amount of precipitates, while the values of V=86% and PKT=2.5% (T1) did not formed precipitate in the wine. This treatment also originated highest amounts of potassium ion in the grapes and must (Table 5).

4. Conclusion

The results suggest that the soil conditions tested in this study had a great effect on the grape and wine quality and possibly in the wine stability. However to recommend the better soil exchange complex saturation with base and percentage of exchangeable potassium in the

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