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Article

Decreased Leaf Potassium Content Affects the Chemical Composition of Must for Sparkling Wine Production

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Abstract: The must used to make sparkling wine has a low pH value and moderate sugar content, and its potassium content can have a strong influence. An excess of potassium often leads to an insufficient supply of magnesium, since potassium has a strong antagonistic effect on magnesium, and, consequently, to poorer photosynthesis and a poorer quality of the must. The aim of this study was to determine whether the application of foliar fertilizers based on magnesium, phosphorus, and amino acids could reduce leaf potassium content, affecting the reductions in sugar content and pH value and increasing the total acidity of the must. A fertilizer trial with three replicates was conducted on the cultivar Istrian Malvasia (TCtrl—NPK, TMg—NPK + Agromag (6% MgO), TMgP—NPK + Agromag + Fosforo (30% P_2O_5) i TMgPBS—NPK + Agromag + Fosforo + Bio Prot) in a random complete block design. The NPK fertilizer was applied in the autumn. Foliar fertilization was applied three times during the growing season (31 May, 7 July, and 22 August 2014), and leaf samples were collected for leaf analysis before each application. The results show that foliar fertilization significantly reduced leaf potassium content, especially when treated with magnesium alone (treatment TMg). In addition, foliar fertilization significantly lowered the pH and increased the sugar content of the must. The results obtained in this research give a scientific contribution to the creation of fertilizer treatments for vines with a positive effect on the basic chemical composition of the base wine and provide a good basis for further research in reducing the use of certain enological practices during production.

Keywords: grapes; foliar fertilization; pH value; sugar; total acidity

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1. Introduction

Sparkling wines are produced by a second fermentation of the base wine using two techniques: the method of fermentation in tanks and the method of fermentation in bottles [1,2]. Sparkling wines are becoming increasingly popular, and in the period from 2002 to 2018, production increased by 57%, an average of 3% per year. In 2018, global sparkling wine production reached 20 million hectoliters (mhL) for the first time. Sparkling wine production accounts for an average of 7% of global wine production, and with a record high of 8% in 2017, the EU has represented between 70 and 80% of global production volume. The steady growth trajectory since then—with an average annual growth rate of 3%—peaked in 2018, when global sparkling wine consumption reached 19 mhL. In 2018, the volume of global exports accounted for 9% of the total wine exported worldwide, representing 20% of the total value of exported wine [3]. The same sources indicate that sparkling wines were increasingly produced in warmer and drier regions of the world, so it is difficult to achieve satisfactory parameters in the chemical composition of the base wine, which limits their production despite the adaptation of agricultural techniques and earlier harvest dates [4].

Climate and soil generally have a great influence on the quality and style of wines. In the period from flowering to harvest, average minimum temperatures of 18 °C and at least 300 mm of water are required for white grapes to ripen [2]. Soil management, including improvement of nutrient status, affects wine quality [5]. Red soils are abundant in K and moderate in Mg and P [6]. Agrotechnical practices in the vineyard are of great importance for the chemical composition of the must (TA, pH, and sugar) in the production of sparkling wines [7]. However, the authors of this study did not investigate the effects of foliar fertilization on leaf K decrease and the effects of this decrease on the chemical composition of must in the production of sparkling wines to achieve the desired characteristics.

The idea of the possible positive effect of foliar fertilization with magnesium (Mg), phosphorus (P), and amino acid-based biostimulants (BS) on the K decrease of leaves and, consequently, on the chemical composition of must arose from knowledge of the strong antagonistic effects of K and Mg. Potassium blocks the uptake and, especially, the translocation of magnesium in the plant much more than vice versa [8]. Since the concentrations of potassium and magnesium ions in the soil solution are different, they also require different transfer systems through the root biological membranes. One possible reason for the reduced uptake of magnesium could be that some Mg^{2+} ion carriers (such as CNGC family proteins) can also transport other ions, such as K^+ ions [9]. Therefore, in soils with excess K or excessive application of K^+ fertilizers, Mg deficiency often occurs due to their antagonistic relationship and large K/Mg ratios [9,10]. Foliar application of Mg decreases the K/Mg ratio [10]. The K/Mg ratio is often much more important for the quality of the must than the Mg content itself as it affects organoleptic characteristics, pH, and total acidity [11].

Since each of these elements has specific physiological functions in the plant, a good balance is required. In plants, K^+ influences numerous aspects such as growth, the activation of many enzymes responsible for metabolism and biosynthesis, tolerance to biotic and abiotic stresses, and the neutralization of organic acids [8,12]. On the other hand, low K content can reduce sugar concentration [13]. Excessive K^+ concentrations in grape berries have a negative effect on wine quality, mainly because they reduce tartaric acid content, which, in turn, leads to an increase in the pH of the grapes, must, and wine [14]. In warmer climates, K^+ ions accumulate and increase during grape ripening, leading to excessive neutralization of organic acids [15]. One possible reason for this is high temperatures, which promote the consumption of malic acid as a respiratory substrate, resulting in low total acidity in the must and disrupting pH control, which leads to wine instability. Excessive K fertilization leads to Mg deficiency [16]. Increasing the K content in the leaves by foliar K fertilization does not significantly affect the content of TA and the pH of the must, while the sugar content decreases [17]. Increased magnesium content affects decreased potassium uptake, while another study reported an increase in Mg content in leaves with foliar Mg fertilization without significant effects on K content [18,19]. Since Mg is involved in numerous physiological and biochemical processes and activates a large number of enzymes, it is important for the photosynthetic activity of the plant. Due to its relatively small ionic radius and large hydration radius, Mg binds weakly to the soil and is easily leached from the soil [9]. The same authors noted that Mg deficiency is a growing problem in agriculture, especially in acidic soils that are highly saturated with cations, and especially in areas with high rainfall. Moreover, Mg deficiency occurs in sandy soils with high rainfall, poorly drained soils, and vineyard soils with a strong alkaline reaction [20]. For this reason, foliar fertilization with Mg is a good measure to improve the Mg status of plants since Mg administration increases the chlorophyll concentration in the leaf and the vegetative yield [9]. Magnesium is incorporated into the cell wall in the form of Mg pectinate and as Mg oxalate, which neutralizes excess acidity. It is also important for P nutrition. Phosphorus is an important structural component of nucleic acids and membrane lipids, activates enzymes and metabolic intermediates, and provides reusable energy storage in

ATP, making it essential for photosynthesis, glycolysis, and plant respiration, and thus for sugar metabolism [21,22]. Excess P can also cause K deficiency [23]. Biostimulants containing amino acids and nitrogen have a positive effect on the mineral content and organoleptic characteristics of wine [6]. The optimal content in grapevine (cv. Tempranillo) leaves at maturity is 0.767–0.907% K, 0.384–0.455% Mg, and 0.148–0.163% P [13].

Base wines are made from must with a chemical composition that is different from still wines, which must have a lower pH, a higher TA, and a moderate sugar content. A high pH in the must is not desirable because it directly affects the wine by reducing the quality and stability of the color, negatively affecting the freshness and aging potential, and giving the wines an inharmonious taste [24]. These negative effects are undesirable in the production of base wines for sparkling wine because sparkling wines need freshness and a long aging potential. Preferably, base wines have a pH between 2.90 and 3.10 [4]. For white wines, winemakers often recommend pH values between 3.10 and 3.20, and if the pH is too high (>pH 3.4), it may be a sign that the grapes are overripe. It is generally known that the activity of the enzymes involved in central carbon metabolism is pH sensitive, which could account for the pH-related changes in the production levels of several organic acids in wine [25]. The high K content in the leaves is precisely related to the high pH of the must [26]. Excessive K content in grapes results from insufficient or excessive potassium fertilization in the vineyard, which leads to the blockage of magnesium (Mg) uptake and thus of photosynthesis [27]. As a result, there is an unfavorable ratio of tartaric and malic acids and reduced total acidity. A negative correlation was found between Mg and total acidity and between P and total acidity and a positive correlation between Mg and sugar [28].

Higher total acidity levels are important in base wines [29]. The total acidity of grapes, must, and wine consist largely of organic acids, and these have a great influence on freshness and the perception of other flavors, such as sweet and bitter, in the production of sparkling wines [30,31]. In base wine, a total acidity of 6.00–8.00 g/L is desirable, and this level is reduced by the precipitation of potassium bitartrates during must vinification [4]. It is therefore important to ensure a higher total acidity of the must, which could be affected by a decrease in K and an increase in Mg. With a tendency to increase the total acidity and sugar, the application of Mg affects the sugar content, given that Mg is an integral part of chlorophyll, which is responsible for photosynthesis, and without which there is no sugar production [10].

The sugar in must arrives from the grapes, where it is formed as a product of photosynthesis and is used by yeasts during fermentation to produce alcohol and other byproducts [30]. Since a high alcohol content in base wines is not desirable, and an additional 1.3–1.5% alcohol is formed during secondary fermentation, it is important that the sugar content in the must is not too high [2]. The preferred alcohol content in the base wine is up to 11.5%, which means that the sugar content in the must should not exceed 87.60 °Oe [4]. In the Champagne region, the alcohol content is generally between a minimum of 8% and 11%, which is more in line with the winemaker's personal choice [32].

Correction of pH and total acidity can be made later in the production process. However, such interventions increase production costs and do not guarantee long-term success in achieving the desired characteristics. Lower sugar content can be achieved by harvesting earlier, but then the grapes may have an unfavorable malic-to-tartaric-acid ratio. It is desirable that the must has more tartaric than malic acid. The reason for this is that malic acid is associated with the sharp and metallic taste of wine and is usually associated with unripe notes or notes of green apple. Malic acid can account for up to half of the total acidity at harvest time and tends to decrease as the grapes ripen [33].

Therefore, the objective of this study was to determine the effects of foliar fertilization with magnesium, phosphorus, and amino acid-based biostimulants on leaf K decline and must chemical composition in order to provide scientific bases for fertilizer design for this narrowly specialized type of enology.

2. Materials and Methods

2.1. Vine, Soil, and Climate

The experiment was conducted in 2014 with the white cultivar 'Istrian Malvasia' (*Vitis vinifera* L.), clone VCR 115, on SO4 rootstock. 'Istrian Malvasia' is considered a Croatian native variety, cultivated throughout the Istrian peninsula to the Italian region of Friuli [34]. Economically, it is the most important native white wine variety in Croatia (9.1% of all vineyards in Croatia). According to the latest data, 1688.85 ha of 'Istrian Malvasia' have been planted in Croatia [35] and 738 ha in Slovenian Istria [36]. In recent years, new producing countries have emerged, which recorded a significant increase in their sparkling wine production in the period 2008–2018 [3]. In many of these countries, native varieties of wine are increasingly used for production of sparkling wines in order to offer on the market something different and unique as well as products with local character. For this reason, 'Istrian Malvasia' was selected for the experiment as one of the native varieties of Croatia, which is increasingly recognized in the world, and from which high-quality wines and sparkling wines are produced.

At the time of the experiment, the vineyard was in full yield (year of planting 2009) and was located in the western part of Istria, Višnjan municipality, Croatia (coordinates: X = 45.143018, Y = 13.423322). The average altitude is 101 m, the slope of the terrain is about 3%, the direction of the rows in the vineyard is east–west, without irrigation systems. The method of training was double Guyot, with a load of 22 buds per vine. All vines were of uniform health and vigor. The vineyard is used exclusively for growing grapes for the production of sparkling wines.

The soil at the site is red soil ("terra rossa", typical Mediterranean soil). The chemical properties of the selected soil were determined as follows: soil reaction (pH) [37], humus [38], total nitrogen [39], plant-available phosphorus (P), and potassium (K) [40]. Plant-available P content was determined using a spectrophotometer (UV-1800, Shimadzu, Kyoto, Japan), while plant-available K content was determined using a flame photometer (M410, Sherwood Scientific, Cambridge, UK). Magnesium content was determined using ICP-OES technique (ICPE-9820, Shimadzu, Kyoto, Japan) after microwave digestion (Ethos up, Milestone, Bergamo, Italy) [41].

The selected soil was poor in phosphorus (<1.0 mg/100 g of soil), rich in potassium (21.25 mg/100 g of soil), and moderately rich in magnesium (14.0 mg/100 g of soil), and with acid reaction (pH_{H2O} 6.37–6.40) (Table 1).

Table 1. Chemical soil properties of selected soil.

Soil Property	Depth, 0–30 cm	Depth, 30–60 cm
pH_{H2O}	6.40	6.37
pH_{KCl}	5.86	5.51
% humus	2.01	2.10
% N_{total}	0.22	0.22
mg P_2O_5/100 g soil	<1	<1
mg K_2O/100 g soil	21.50	21.25
mg Mg/100 g soil	14.0	14.0

The climate is temperate Mediterranean. In 2014, monthly precipitation was higher than the multi-year average (1981–2010) in all months, with the largest deviation in July, with 3.5 times more precipitation (154.3 mm) (Figures 1 and 2). Monthly average temperatures were higher than the multi-year average in March, April, and June and lower in July, while they were similar to the multi-year average in the other months. The average temperature in the period from flowering to harvest was 20.22 °C and the total precipitation in this period was 500.70 mm.

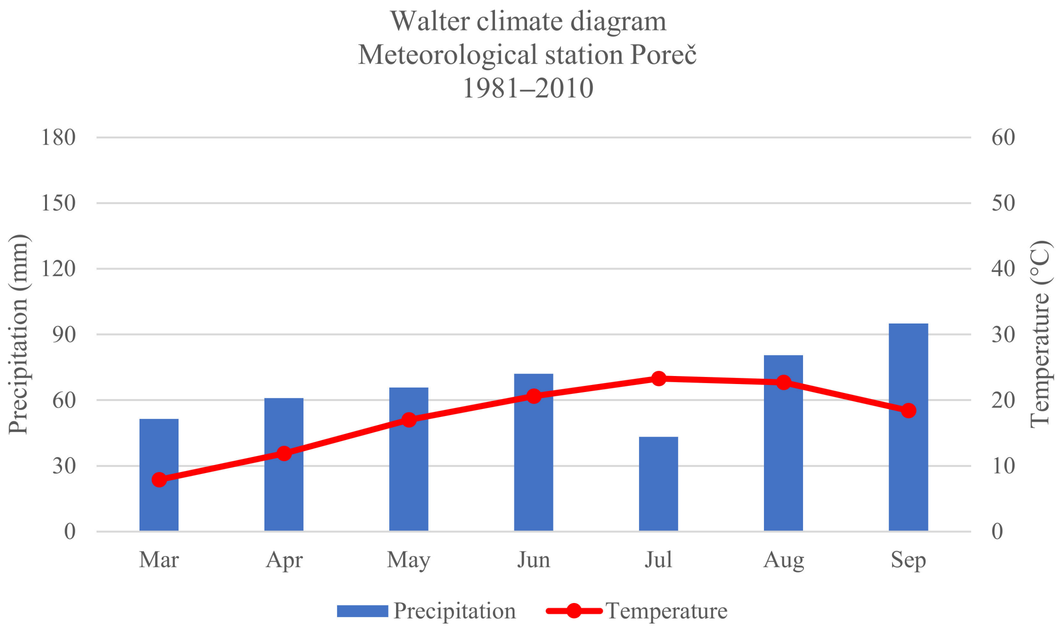

Figure 1. Walter climate diagram for meteorological station Poreč, multiyear average (1981–2010).

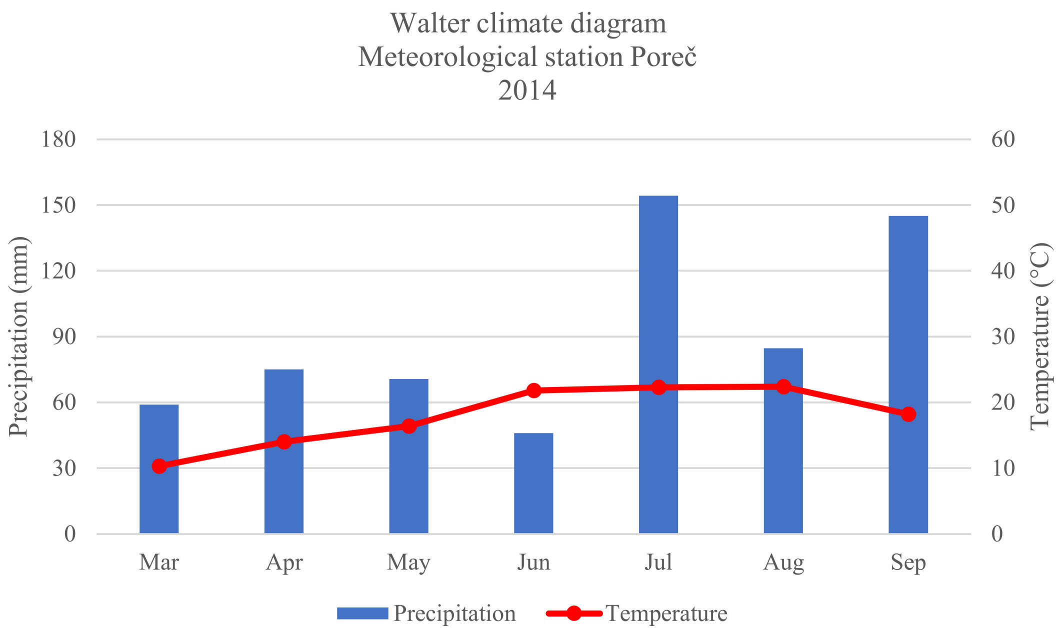

Figure 2. Walter climate diagram for meteorological station Poreč, year 2014.

2.2. Fertilization Treatments

The study was conducted according to a randomized block layout (RCBD) with basic plots of 14 vines each. Four fertilizer treatments were applied in three replicates: TCtrl (NPK or control without foliar fertilization); TMg (NPK + Agromag with addition of Mg); TMgP (NPK + Agromag + Fosforo with addition of P); and TMgPBS (NPK + Agromag + phosphorus + Bio Prot with addition of biostimulants). In all fertilizer treatments, 500 kg/ha of NPK fertilizer formulation 7-14-21 was applied. TMg also contained a 5 kg/ha magnesium fertilizer Agromag 6L (6% MgO), while TMgP also contained a phosphorus fertilizer Phosphorus 30L (30% P_2O_5) at a rate of 3 kg/ha. TMgPBS was also treated with biostimulants Bio Prot, a liquid fertilizer containing an extract of the algae *Ascophyllum nodosum* at a dose of 2 kg/ha. Bio Prot contains organic nitrogen (4%), organic carbon (12%) and amino acids (lysine 1.3%, aspartic acid 1.7%, glutamic acid 3.2%, hydroxyproline 2.5%, valine 0, 8%, isoleucine 0.5%, phenylalanine 0.7%, histidine 0.3%, threonine 0.3%, proline 4.2%, alanine 2.8%, methionine 0.2%, tryptophan 0.02%, arginine 2%, serine 0.5%, glycine 7.8%, cysteine 0.09%, leucine 1.1%, tyrosine 0.4%). The vines were foliar-treated with the minimum doses recommended by the manufacturer for vineyards.

Foliar fertilization was applied three times during vegetation, on 31 May 2014 during the flowering phenophase, on 7 July 2014 during the berry setting phenophase, and on 22 August 2014 during the veraison stage.

2.3. Leaf Analysis

Grapevine leaves were dried at 105 °C until constant weight in a dryer (ST-360T, INKO, Croatia), and ground and homogenized in laboratory mill (M20, IKA, Königswinter, Germany). After digestion of plant material with HNO_3 and $HClO_4$ in microwave oven (ETHOS ONE, Milestone, Sorisole, Italy), phosphorus was determined by spectrophotometer (Evolutuion 60 S, Thermo Fisher Scientific, Waltham, MA, USA), potassium by flame photometer (Jenway PFP-7, Nottingham, UK), and magnesium by atomic absorption spectrometer (Solar, Thermo Scientific, Abingdon, UK).

Laboratory determinations of phosphorus, potassium, and magnesium levels in the leaf were performed using a standard method for the analysis of plant material [42]. The value was determined for each base plot three times during vegetation and leaf samples were taken immediately before each leaf treatment (31 May, 7 July and 22 August 2014).

2.4. Harvest and Chemical Must Analysis

Harvest was performed at once. During the harvest, the clusters were counted for each repetition and treatment, and weighing was performed for each vine. Weighing was performed with a precision scale (precision scale di SKALA SKY, Digitron d.o.o. Buje, Croatia).

The analysis of the basic chemical composition of the must (pH, TA—total acidity and sugar content) was made within the wine laboratory winery Pjenušci Peršurić d.o.o. Must samples were taken after grape processing for each treatment, with three repetitions in duplicate. For the needs of the analysis, 300 mL of must was taken for each sampling.

The pH value was determined by a digital pH meter (Portable meter ProfiLine pH 3110, Xylem Analytics Germany Sales GmbH & Co., Weilheim, Germany), for which the must was tempered to 20 °C. Sugar content was determined by digital refractometer (WM-7, Atago Co. Ltd., Saitama, Japan). All digital devices were previously calibrated and serviced by an authorized service center. The content of total acidity in the must was determined by titration in a sample of 10 mL in which 1 drop of bromothymol blue indicator was added. The prepared 7.5 M sodium hydroxide solution (NaOH) was gradually added until the color of the sample changed to blue–green. The read value of 7.5 M NaOH consumption in this case represented the content of total acidity g/L in the must. The basic chemical composition of the must (pH, TA—total acidity and sugar content) was determined according to the OIV methods for must and wine analysis [43].

2.5. Statistical Analysis

The effects of foliar fertilization on leaf P, K, and Mg content and basic chemical properties of must were statistically compared using the RCBD model of analysis of variance (ANOVA). To test the differences in the mean values of the effects, Tukey's test was performed. Statistical analysis was performed using SAS OnDemand for Academics (SAS Institute Inc., Cary, NC, USA).

3. Results

3.1. Leaf Analysis

The results showed that foliar fertilization had a significant effect on K content in leaves, while there was no significant effect on P and Mg content (Table 2).

Table 2. Influence of foliar fertilization on the content of phosphorus, potassium and magnesium in leaves.

Property	*p*-Value	Significance
P	0.0980	ns
K	0.0013	**
Mg	0.1975	ns

ns not significant; ** significant at 0.01 level.

In terms of statistical significance, the lowest potassium content was found in the TMg treatment where the average value was 0.826% K, while the highest value was 1.053% K in the TCtrl treatment, the treatment without foliar application. The TMgP treatment had an average value of 0.878% K, while TMgPBS had a value of 0.968% K. It is undeniable that foliar potassium levels decreased with foliar fertilizer application, especially in the TMg treatment (Figure 3).

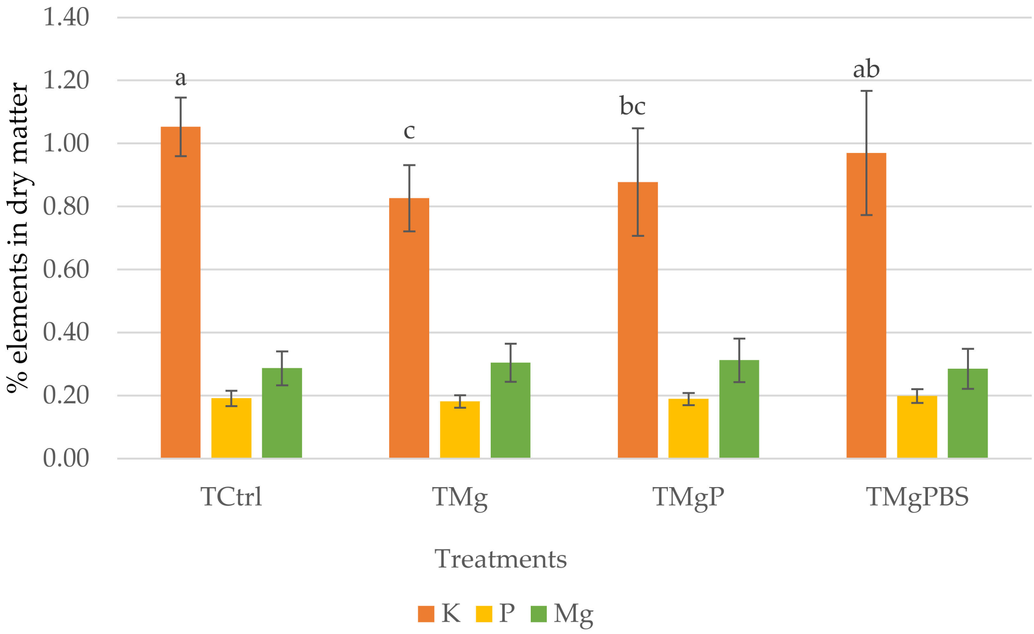

Figure 3. Leaf content of K, P, and Mg in % based on dry matter by treatments. (TCtrl—NPK, TMg—NPK + Agromag (6% MgO), TMgP—NPK + Agromag + Fosforo (30% P_2O_5) and TMgPBS—NPK + Agromag + Fosforo + Bio Prot). Bars with no common letters are significantly different according to Tukey's HSD test ($p \leq 0.05$), Error bars indicate standard deviation (n = 12).

Phosphorus values did not differ significantly and ranged from 0.182 to 0.199%. Magnesium values in leaves did not differ significantly, but a trend toward a slight increase in Mg content was determined in TMg, with 0.304% Mg, and in TMgP, with 0.312% Mg compared to TCtrl (0.287%) (Figure 3).

In this study, the highest K/Mg ratio was determined in the TCtrl treatment (3.67) without foliar fertilization, while the most favorable ratio was determined in the TMg treatment (2.71) when only Mg was applied. K/Mg ratio in TMgP was 2.81 and in TMgPBS was 3.39.

3.2. Yield

No significant differences in yield and number of clusters were determined (Table 3), but a visible trend of increasing yields with respect to the treatments was determined. The TCtrl treatment had the lowest yield, while the TMgP treatment had the highest yield (Figures 4 and 5).

Table 3. Influence of foliar fertilization on yield and number of clusters.

Property	*p*-Value	Significance
Yield	0.9880	ns
Number of clusters	0.2433	ns

ns not significant.

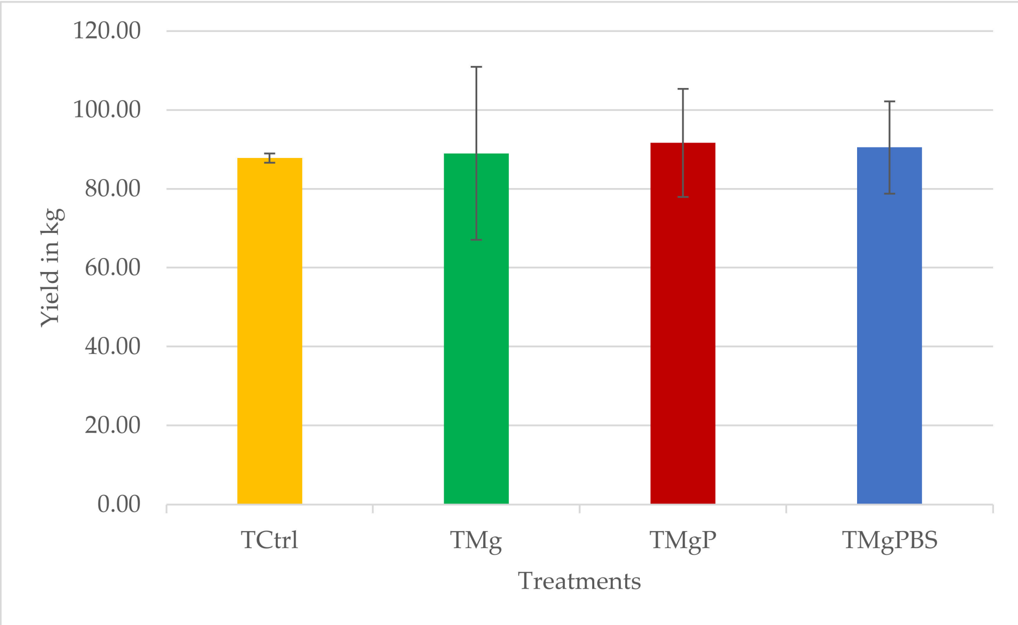

Figure 4. Yield in kg by treatment. (TCtrl—NPK, TMg—NPK + Agromag (6% MgO), TMgP—NPK + Agromag + Fosforo (30% P_2O_5) i TMgPBS—NPK + Agromag + Fosforo + Bio Pro), Error bars indicate standard deviation (n = 3).

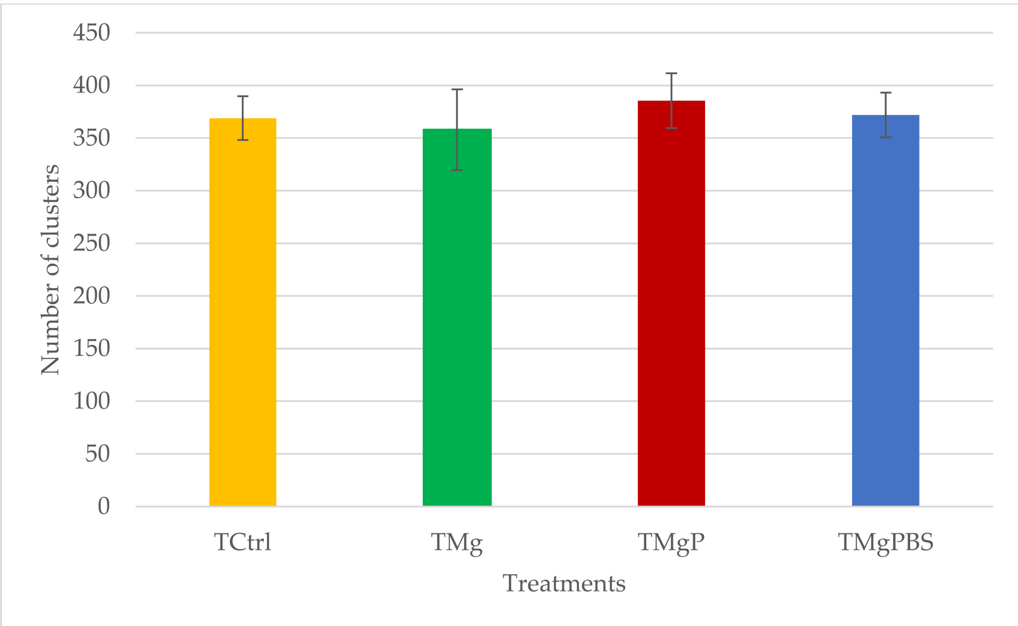

Figure 5. Number of clusters by treatment. (TCtrl—NPK, TMg—NPK + Agromag (6% MgO), TMgP—NPK + Agromag + Fosforo (30% P_2O_5) i TMgPBS—NPK + Agromag + Fosforo + Bio Prot), Error bars indicate standard deviation (n = 3).

3.3. Chemical Must Analysis

Based on the research conducted on the influence of foliar fertilization on the chemical properties of the must, it was found that foliar fertilization significantly influenced the sugar content and pH of the must, while the total acidity (TA) was not significantly affected (Table 4).

Table 4. Influence of foliar fertilization on pH, total acidity, and sugar must.

Property	*p*-Value	Significance
pH	0.0171	*
TA	0.7956	ns
Sugar	0.0001	***

ns not significant; * significant at 0.05 level; *** significant at <0.01; (pH—pH value; TA—total acidity; Sugar—sugar content).

When the differences were tested with Tukey's test for the mean values of the effects of foliar fertilization, it was found that pH was significantly lower in TMg and TMgP (3.00) compared to the control without foliar fertilization, TCtrl (3.05), while it was 3.03 in TMgPBS (Figure 6).

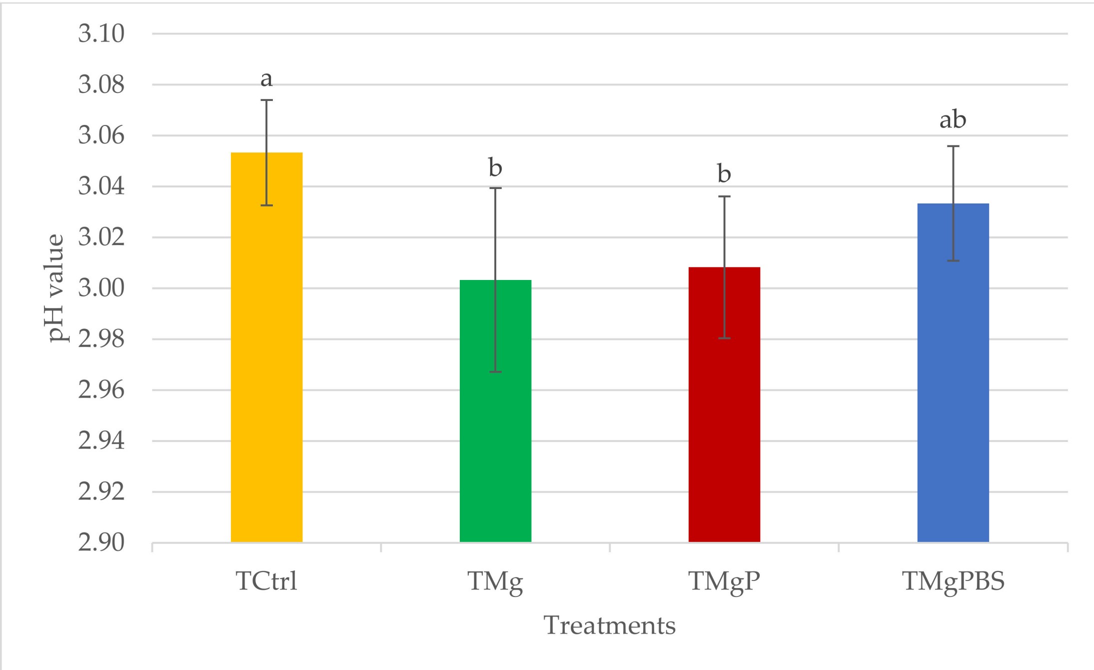

Figure 6. pH of must by treatment. (TCtrl—NPK, TMg—NPK + Agromag (6% MgO), TMgP—NPK + Agromag + Fosforo (30% P_2O_5) i TMgPBS—NPK + Agromag + Fosforo + Bio Prot) Bars with no common letters are significantly different according to Tukey's HSD test ($p \leq 0.05$), Error bars indicate standard deviation ($n = 6$).

Figure 7 shows the results of the influence of foliar fertilization treatments on the content of TA in the must. From this it can be seen that the values obtained for total acidity are quite uniform, ranging from 13.70 (TCtrl) to 13.91 g/L (TMgP).

The study showed that foliar fertilization treatments have a positive effect on increasing sugar content. In terms of statistical significance, the highest sugar content was determined in TMgPBS (76.67 °Oe). In this case, as for pH, the same reading was determined in the TMg and TMgP treatments, 74.33 °Oe, while in the TCtrl treatment, 72.17 °Oe was determined (Figure 8).

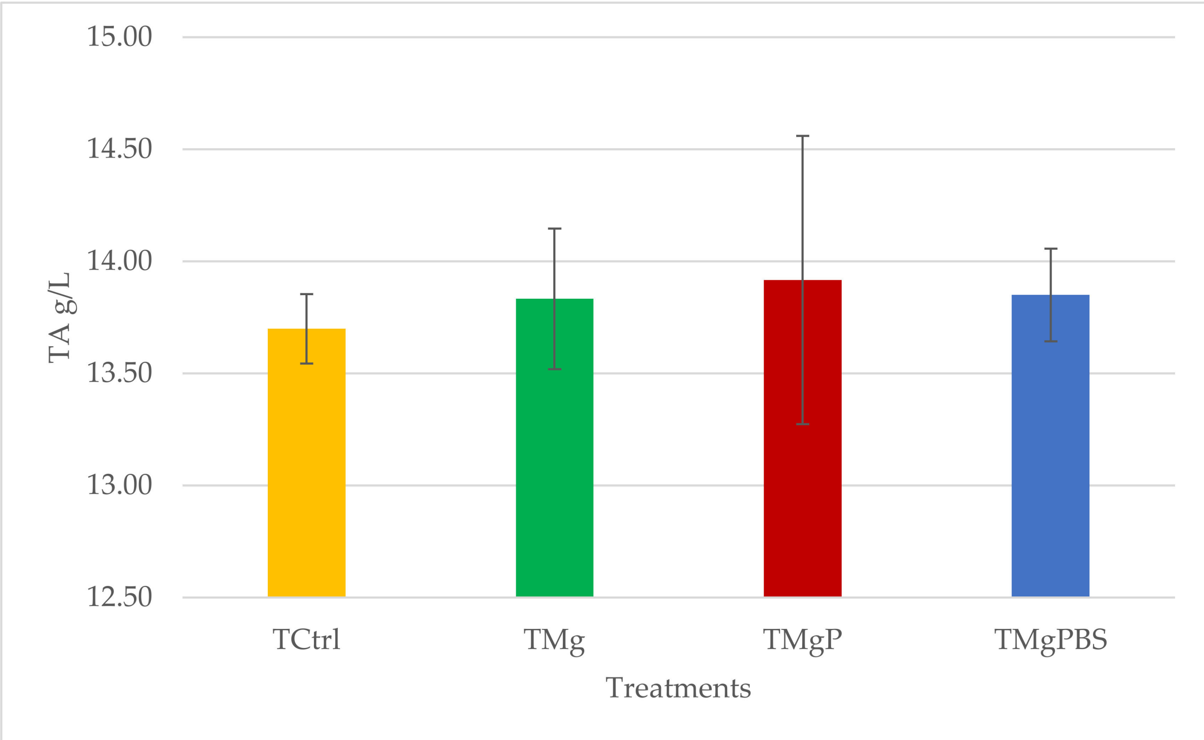

Figure 7. Total acidity (TA) in the must by treatment. (TCtrl—NPK, TMg—NPK + Agromag (6% MgO), TMgP—NPK + Agromag + Fosforo (30% P_2O_5) and TMgPBS—NPK + Agromag + Fosforo + Bio Prot), Error bars indicate standard deviation (*n* = 6).

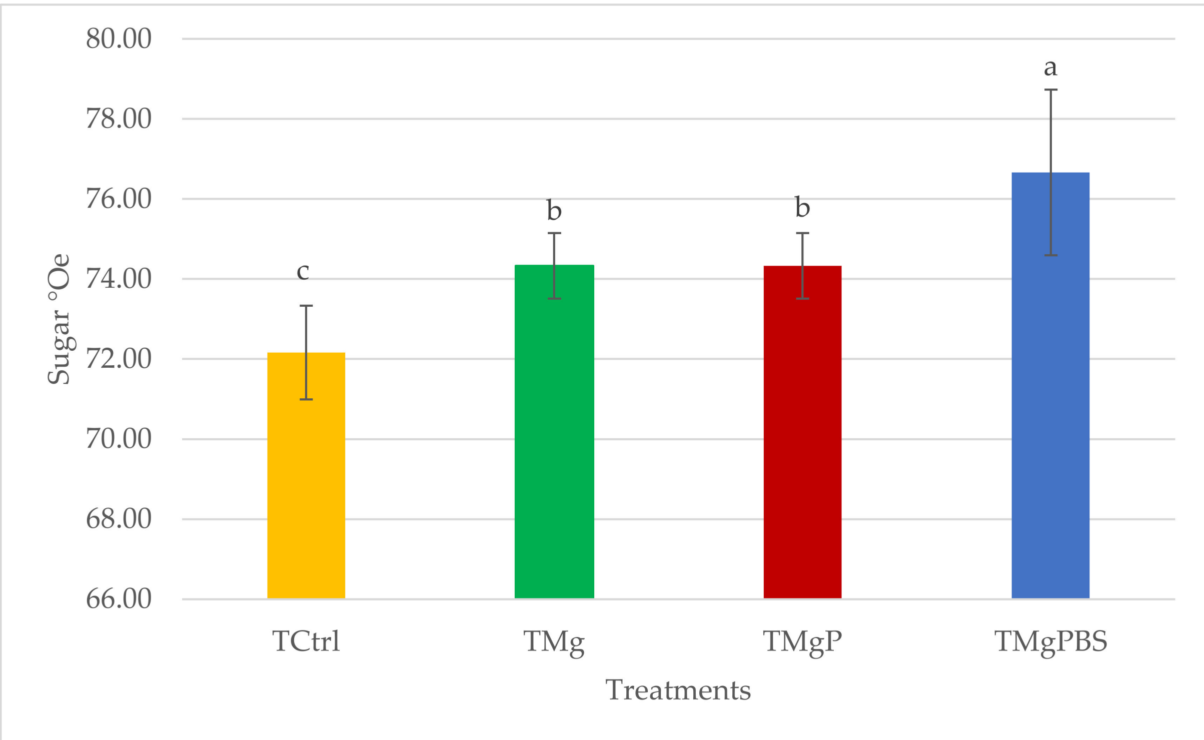

Figure 8. Must sugar by treatment. (TCtrl—NPK, TMg—NPK + Agromag (6% MgO), TMgP—NPK + Agromag + Fosforo (30% P_2O_5) and TMgPBS—NPK + Agromag + Fosforo + Bio Prot). Bars with no common letters are significantly different according to Tukey's HSD test ($p \leq 0.05$), Error bars indicate standard deviation (*n* = 6).

4. Discussion

4.1. Leaf Analysis

The results of foliar fertilization with fertilizers based on magnesium, phosphorus, and biostimulants showed a significant decrease in potassium content in grapevine leaves, which is consistent with the claim that K content in leaves is reduced by targeted Mg administration [18]. This is probably due to the mutual antagonistic relationship between the two elements. However, the obtained results are in contrast with studies that foliar fertilization with Mg had no effect on the potassium content of leaves [19].

Foliar fertilization had a positive effect on the K content in leaves, as the K content in leaves was slightly above the optimum only in the control treatment (1.053% K), while in all other treatments (0.826–0.968% K) the values were in the optimum range (0.767–0.907% K) [13]. Similarly, the Mg content in grape leaves was slightly lower than the optimal range (0.312 and 0.304% Mg, respectively) for TMgP and TMg, while the determined values for TCtrl and TMgPBS (0.287 and 0.285% Mg, respectively) were significantly lower than the optimal range (0.384–0.455% Mg) [13]. TCtrl had a higher K content in leaves, so there was obviously antagonism between these two elements. Although the same amount of magnesium fertilizer was used in TMgPBS as in treatments TMg and TMgP, there is a possibility that TMgPBS, which contains additional nitrogen and amino acids, had a greater leaf mass and thus a higher leaf magnesium requirement. The P content in all treatments (0.182–0.199% P) was higher than the recommended optimal range (0.148–0.163% P) [13].

This study confirms that foliar fertilization of Mg leads to a decrease in the K/Mg ratio, as the highest ratio was obtained in the treatment without foliar fertilization [10].

4.2. Chemical Must Analysis

A significantly lower pH and a more favorable (lower) K/Mg ratio (2.71 and 2.81, respectively) were obtained in the TMg and TMgP treatments, which was due to the fact that the Mg content did not differ in the treatments, while the K content decreased significantly. Thus, the K/Mg ratio was affected by the decrease in K content rather than Mg content [11]. These treatments had significantly lower K content in the leaves, which also contributed to a decrease in pH. In addition, the highest pH in TCtrl was found to have the highest K in the leaves [27]. Although the differences between the measured pH values are small, they are statistically significant, indicating that the effects of higher doses of foliar fertilizers need further investigation. High must pH is increasingly common, especially at low latitudes, and acidification may become an unavoidable enological treatment, but the addition of tartaric acid is often used with inconsistent results [44]. The organoleptic perception of wines can be significantly affected by slight changes in wine pH (up to 0.05 units), along with changes in total acidity (0.2–0.5 g/L). [45]. In the experience of one of the authors, who also produces sparkling wine, even very small decreases or increases in pH (as in this case, 0.05) can have an important effect on the further course of vinification. Indeed, it is known from experience that the pH changes during vinification under the influence of various enological treatments. Thus, if the pH in the must is already 0.05 higher than the desired value of 3.10 [4], further processes may cause the pH to increase further and become too high above the desired value, thus further increasing production costs and requiring additional enological treatments.

Although no significant difference was found for TA, all fertilizer treatments had high total acidity, which was probably strongly influenced by the weather conditions in 2014, and the trend of increasing TA by applying Mg foliar fertilizer was confirmed [10]. In the studied year, more than 1.5 times the minimum rainfall requirement for grapes was observed in the period from flowering (May) to harvest (September), and average temperatures were above the minimum required for white grape ripening (18.00 °C) [2]. It can be concluded that the increased precipitation may have contributed to greater leaching of Mg from the soil as well as to the occurrence of possible Mg deficiency [9,20], since the red soil type is moderately supplied with Mg [6].

In this study, relatively higher acidity was found in all treatments where Mg fertilizer was applied through the leaves compared to the treatment without Mg fertilizer. The highest relative value was obtained in TMgP, where P was also administered with Mg. The results obtained are in contrast to the claim that an increase in Mg and P content in leaves leads to a decrease in total acidity [29]. Although Mg leaf treatments relatively increased TA content, a statistically significant difference was not found [6].

In this study, it was found that the application of foliar fertilizers based on Mg, P, and BS had a highly significant effect on sugar content in the rainy vegetative conditions. The lowest sugar content was found in TCtrl treatment, with the highest K content in leaves, which is consistent with the claim that increasing K content in leaves leads to a decrease in must sugar [17]. However, these results contradict the claim that low K levels lead to a decrease in sugar concentration [13]. In our previous research, some of these treatments (treatment with Mg and P, and treatment with Mg, P and biostimulants) in dry years significantly affected the maintenance of sugar content within optimal values [46]. In all treatments where foliar fertilization was applied, there was an increase in sugar content. The results are partially consistent with the statement that there is a positive correlation between Mg and sugar [28]. Moreover, the Mg content in the leaf was the lowest in the TMgPBS treatment, but probably the biostimulants had a higher influence on the sugar content in this treatment [6,25]. The obtained sugar content indicates that the base wine would have an alcohol content ranging from 9.1% (TCtrl treatment) to 9.7% (TMgPBS). These results are consistent with the rank of desirable alcohol content in Champagne [31]. It can be concluded that, in this case, the most desirable treatment is TMgPBS because the potential alcohol content of this base wine is closer to the preferred alcohol content of base wines between 10.0 and 11.5% [4].

Thus, foliar fertilization with Mg, P, and biostimulants had a positive effect on the chemical characteristics of the must. In this study, the recommended minimum doses of foliar fertilizer for vineyards were used. In order to obtain an even better positive effect on the chemical properties of must for sparkling wine production, it is suggested to consider the use of higher fertilizer doses.

5. Conclusions

From the results obtained, it can be concluded that foliar fertilization based on Mg, P, and BS had a positive effect on decreasing the potassium content in the leaves, lowering the pH, and increasing the sugar content in the must. In addition, it was found that the application of foliar treatments increased the sugar content in the must, which is not desirable in the production of base wines for sparkling wines in warm regions. However, this effect of the treatments on increasing sugar content in must could be applicable when designing fertilizer treatments in colder and wetter years or regions, such as Champagne.

Overall, the results and growers' requirements for chemical composition of must for sparkling wine production lead to the most desirable treatment being TMgP, which has lower but not the lowest potassium content in leaves, and with TMg the lowest pH, highest total acidity, and most desirable sugar content. These treatments have the most favorable K/Mg ratio (2.71–2.81). This approach to the application of foliar fertilization, aimed at correcting the chemical composition of the must, could reduce the need for corrective measures in the must and wine during the production process. It would be good to conduct this research on other grape varieties to determine the possible influence of the variety or the same variety (Istrian Malvasia) in other regions where it is grown (Slovenia, Italy). Moreover, since the research was conducted in the Mediterranean climatic region in a very specific terroire, it would be desirable to further investigate the effects of fertilization treatments in other climatic conditions in the coming years, since the vineyards in Croatia are also located on the continent.

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