fermentation

Article

The Effect of a Leaf Fertilization Method Using Humic Acids on the Minerality and Chemical Composition of Sauvignon Blanc Wine from the Slovak Wine Region

Martin Bartkovský [1,*], Boris Semjon [1], Ivana Regecová [1], Viera Baričičová [2], Peter Očenáš [3], Lucia Šuľáková [1] and Slavomír Marcinčák [1]

[1] Department of Food Hygiene, Technology and Safety, University of Veterinary Medicine and Pharmacy in Kosice, Komenského 73, 041 81 Kosice, Slovakia; boris.semjon@uvlf.sk (B.S.); ivana.regecova@uvlf.sk (I.R.); slavomir.marcincak@uvlf.sk (S.M.)
[2] Ministry of Agriculture and Rural Development of the Slovak Republic, Dobrovičova 12, 812 66 Bratislava, Slovakia; viera.baricicova@land.gov.sk
[3] Department of Chemistry, Biochemistry and Biophysics, University of Veterinary Medicine and Pharmacy in Kosice, Komenského 73, 041 81 Kosice, Slovakia; peter.ocenas@uvlf.sk
* Correspondence: martin.bartkovsky@uvlf.sk; Tel.: +421-917-124-764

Abstract: The objective of this study was to analyze the minerals transferred to Sauvignon blanc must and wine as an effect of foliar fertilizer application. The mineral composition was determined via atomic absorption spectroscopy. Experimental leaf and berry samples were examined during the phenological grapevine growth phases. A foliar fertilizer mixture (0.5 L/hL) with humic acids (8.51%) and B (0.031 kg) was applied. It was observed that the application of humic acids and boron significantly influenced the quality of Sauvignon blanc wine samples. During the blooming period, there was a statistically significant increase ($p < 0.05$) in P, K, and B in the experimental group. The results showed that using HAs and B in foliar fertilizer significantly ($p < 0.05$) increased the concentration of minerals in the experimental group. However, P and Fe content in the leaves decreased after veraison. After processing the berries in the vinification process, the levels of B in the must (0.71 ± 0.06 mg/kg) and, subsequently, in the wine (0.61 ± 0.06 mg/kg) were significantly ($p < 0.05$) higher in the experimental group. Data showed that the foliar fertilizer significantly increased the concentration of N (176.24 ± 0.02 mg/L) in the experimental must. These changes were also observed in wine samples. In wine, a statistically significant decrease in Ca (82.86 ± 0.29 mg/kg) was observed.

Keywords: minerals; nutrition; fertilization; wine; grape

check for updates

Citation: Bartkovský, M.; Semjon, B.; Regecová, I.; Baričičová, V.; Očenáš, P.; Šuľáková, L.; Marcinčák, S. The Effect of a Leaf Fertilization Method Using Humic Acids on the Minerality and Chemical Composition of Sauvignon Blanc Wine from the Slovak Wine Region. *Fermentation* **2024**, *10*, 651. https://doi.org/10.3390/fermentation10120651

Academic Editor: Manuel Malfeito Ferreira

Received: 5 November 2024
Revised: 5 December 2024
Accepted: 9 December 2024
Published: 16 December 2024

1. Introduction

Viticulture has a significant economic, landscaping, and historical influence on the regions where grape vines are grown; however, it also has an impact on consumers [1,2]. The natural levels of trace elements in wine are typically non-toxic. Agricultural practices could, however, change the quantity of trace elements in vineyards [3,4]. Elements such as Zn, Mn, and Cu have mainly increased due to the use of fertilizers and pesticides to prevent mold growth [5]. The acidity of must and wine can dissolve Cr, Cu, Ni, and Zn from the equipment used during the wine-making process [6,7]. Therefore, the quality of wine needs to be determined not only in terms of the determination of its nutritional value but also in terms of consumer safety [8]. The Slovak wine region is known for producing mono-grape wine varieties that benefit from a specific terroir and soil composition [1,9]. The aim of vineyard fertilization techniques is to replenish soil nutrients to the levels necessary to support the best possible growth of grapevines [7]. The limiting minerals for healthy grapevine production are N, P, K, and Mg. Successful alcoholic fermentation does not depend solely on these minerals. For the grapevine ripening and fermentation process, Cu, Fe, Ca, Co, and Zn are needed as well [5,9]. Minerals such as Fe, Cu, and Mg are not only used during grapevine ripening, but they are also essential for grape cell metabolism, specifically due to their aprotic cofactor function in certain enzymes (e.g., oxidoreductases and kinases). However, the fertilizers and pesticides used in vineyard practices are also responsible for increasing the level of anions, such as phosphates and nitrates, as well as cations, namely, Cu, Zn, etc. [1,4,7,10].

Foliar fertilization is a frequently used method of fertilization. The need for more effective foliar fertilizers has grown in recent years [11,12]. One method to improve the absorption of minerals from foliar fertilizers is to employ humic acids (HAs) [13]. Numerous significant ecological and environmental processes are managed by HA, including stabilizing soil structure, controlling the growth of plants and microbes, and controlling the nitrogen and carbon cycles in the soil [14–16]. Humic acids are low-molecular-mass constituents that form dynamic associations in solution that could be maintained by hydrogen bonds and hydrophobic interactions [2,17,18]. Popescu and Popescu [15] studied the effect of HAs (produced from vermicompost) in three different concentrations (30, 40, and 50 mL/L). Their research presented an ecologically friendly foliar spray that caused a rise in ATP synthesis and activity in the root cells as well as increased growth, yield, and total soluble solids. These results were in contrast to Aljabary et al. [13], who stated that organic fertilization with HAs (20 mg/L) increased the percentage of K, N, and P in the petiole leaves of grape seedlings. The percentage of protein was also increased in the leaves. By increasing grapevine root efficiency and absorption, HAs increased the concentration of macronutrients in the leaves and the amount of anthocyanins in the juice [12,19]. According to Eman et al. [20], using HAs instead of nitrogenous mineral fertilizer on Thompson Seedless grapes decreased the amount of nitrogen in the leaves without affecting the amounts of K and P. Changes in N content following HA treatment were the main focus of work performed by Aljabary et al. [13]. The maximum amount of HAs (9 mg/vine), however, caused the leaves' N, P, K, and Zn contents to drop significantly.

The aim of this study was to compare the mineral content and absorption of minerals in the leaves, as well as the transfer of minerals to must and wine after the application of a foliar fertilizer containing HAs and boron (B). The control group was fertilized using a standard fertilizer (NPK fertilizer incorporated into the soil by plowing) and analyzed alongside an experimental group (foliar fertilizer application). The impacts of foliar fertilizer administration on mineral transit into wine and nutrient absorption were the primary focus of the study.

2. Materials and Methods

2.1. Vineyard Parameters and Growth and Climatic Conditions

The experiment was conducted in an experimental vineyard located in the Eastern Slovak wine region (48°46′ N, 22°13′ E, 126 m above sea level). For both the control and experimental groups, four hundred grapevines were monitored. Vine rows were spaced 2.0 m apart, with individual vines 1.2 m apart from each other and oriented in a southwest direction. The cultivar was Sauvignon Blanc (clone 530) grafted onto a TELEKI 5C (crossbreed of Vitis berlandieri × Vitis riparia) basis. Soil management treatments were established in the autumn of 2019. Grapevines were trained using the Guyot pruning system at a height of 0.6 m from the ground. Every vine was consistently pruned to seven nodes per meter in a row. The predominant soil type was volcanic andesite. The climate had a distinctive continental character (Central European steppes). During the experiment, the weather conditions were monitored. During the experiment, the average annual temperature was 12 °C, annual rainfall was 682 mm, and the average length of sunshine was 2088 h per one-year period (from October 2020 to October 2021) (Slovak Hydrometeorological Institute in Košice).

During the spring of 2021 (February), the soil of the control group's area was fertilized. The fertilizer was applied using gravity with a pressure of 1 atmosphere. With a plow, the fertilizer was blown on two sides into a furrow dug below the surface of the soil 40 cm deep. The plowshare distributed the granulated fertilizer up to a width of 120 cm. The fertilizer consisted of N (12%), P (6%), and K (18%). The dose of fertilizer before sprouting was 50 g/m. Pest control, soil management, and other viticultural operations were conducted according to standard practices. Pest control was controlled according to the recommendations of the Central Control and Testing Institute of Agriculture in Bratislava, Slovakia. The spraying was carried out equally in both the control and the experimental groups. In the given year, spraying was used against *Plasmopara viticola* and *Uncinula necator*. For pest control, Polyram WG (Metiram 700 g/kg, Floraservis, Bernolákovo, Slovakia) was used against *Plasmopara viticola*. The Luna Experience (Fluopyram 200 g/L, tebuconazole 200 g/L; Bayer Crop Science, Bratislava, Slovakia) was used against *Uncinula necator*. Subsequently, soil samples were taken after soil fertilization. Soil samples were taken before flowering in both experimental groups, control and experimental groups, respectively. In the experimental group, the soil sample was taken after the application of the foliar fertilizer. After the grape harvest (October 2021), soil samples were taken from the control and experimental groups for mineral content determination. Individual soil samples were taken using a spade from approximately 10 places distributed in a checkerboard pattern over the entire area. The vertical hole was excavated with a spade to a depth of 1.0 m. The top layer and the side edges of the soil layer were removed with a knife. Next, the collected soil samples were mixed, and the stones and plants were removed. For the leaf fertilization technique, a mixture of humic substances and B obtained from the Agroculture Bio Inc. company (Nitra, Slovakia) was applied. This mixture contained Co, Cu, Fe, Mn, Mo, Zn, K, and N. According to the manufacturer's instructions, 500 mL of fertilizer should be added per 100 L of water. Fertilization was conducted in three stages. The first application was after the creation of a sufficient leaf surface area, the second application was before flowering, the third was after veraison, and the last one was during intensive berry growth. The mineral composition of the leaf fertilizer is presented in Table 1. Analysis of the leaf fertilizer composition was provided by Morava Inc. Laboratories (Studénka, Czech Republic) according to ISO standards (Table 1). During the harvest, the yield (kg/plant), cluster weight (g), berry volume (mL/100 berries), sugar content (°Brix), and titratable acidity (g/L) were measured (Figures 1 and 2). Grapevine berries from the experimental and control group rows were collected and weighed manually (100 berries). Samples were taken diagonally from the control and experimental group areas. During the harvest, approximately 0.65 tons of berries were collected from each experimental group.

Table 1. The mineral composition of the utilized foliar fertilizer.

Foliar Fertilizer Composition	
Boron (mg/kg)	31,200
Cobalt (mg/kg)	<2.50
Copper (mg/kg)	<2.50
Iron (mg/kg)	17.8
Manganese (mg/kg)	<2.50
Molybdenum (mg/kg)	<0.50
Zinc (mg/kg)	<2.50
Potassium (K_2O) (mg/kg)	0.29
Total nitrogen (%)	4.32
Humic acids (%)	8.59

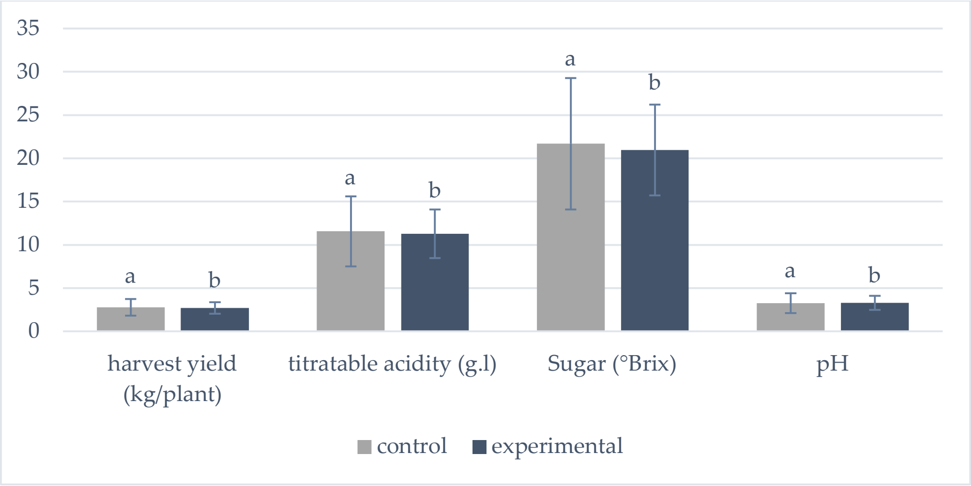

Figure 1. The results of yield parameters of produced grapes (means ± SD). ^{a,b}—values are statistically significant (Student's *t*-test, $p < 0.05$).

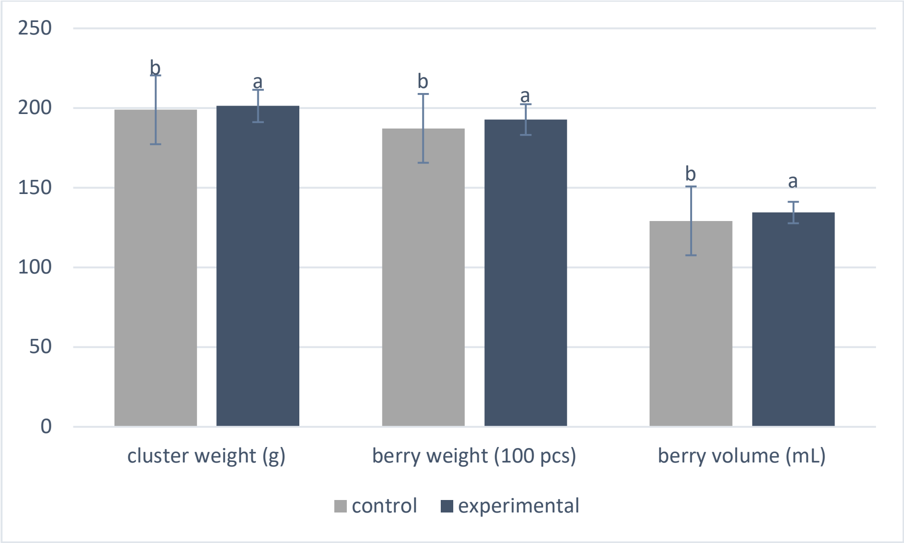

Figure 2. Basic grape quality parameters (means ± SD). ^{a,b}—values are statistically significant (Student's *t*-test, $p < 0.05$).

2.2. Leaf Mineral Content Determination

During the 2021 season, the mineral content of the leaves was measured in the petioles at veraison. For each treatment, six samples were examined. For every sample group, forty healthy leaves from the bunch zone were gathered. Leaf samples were kept in the dark in a refrigerator. Analysis of the nutrient content was performed less than a day from the following collection. The leaves were kept in a cold environment at 4 °C ± 0.1 °C. Following methods outlined by Horneck and Miller [21], the N concentration was determined via the Kjeldahl method (VELP UDK159, Velp Scientifica, Monza e Brianza, Italy). Using an iCAP 7400 ICP-OES Analyzer (Thermo Fisher Scientific, Waltham, MA, USA), atomic absorption spectrometry was used to measure the content of P, K, Ca, and Mg. The leaves were rinsed with distilled water in order to remove any surface contamination and dried at 60 °C in an electric oven. The dried leaf samples were homogenized in a mortar using a pestle. The powdered samples (0.25 g) were digested in 6.5 mL of trichloric acid (1%). The solution was filtered with filter paper No. 1 and diluted up to 50 mL with distilled water [22]. Standard working solutions for each element were prepared to establish the calibration curve. The calibration and spike solutions were prepared using 1000 µg/g single-element solutions (SPEX CertiPrep Group, Metuchen, NJ, USA). The solutions were prepared using 18 MΩ ultra-pure distilled water and trace metal-grade HNO_3 (67–69%, Fisher Chemical, Loughborough, UK), as well as analysis-grade ethanol (99.8% Fisher Chemical, Loughborough, UK). The final concentration of HNO_3 for each solution was 0.1%. The pump speed was set to 50 rpm. The nebulizer gas flow (0.55 L/min) and coolant gas flow (12 L/min) were set according to a study by Assendorf [23]. The plasma ignition and warm-up period were set up 15 min before the measuring began. The analyzer optimization was performed directly before analysis.

2.3. Chemical Analysis of Wine

The winemaking process was monitored by measuring the sugar content (°Brix) of the must and young wine until a specific dryness (4 g/L) was achieved. The wine samples were produced via the reduction method—without the presence of oxygen. For the wine production, 900 L stainless steel tanks were used. The yeast culture used for fermentation was *Saccharomyces cerevisiae* at a dosage of 30 g/100 L (Oenoferm Elégance, ERBSLOH, Geisenheim, GmbH, Geisenheim, Germany). Yeasts were controlled by EU Commission regulation No. 934/2019. After fermentation in the steel tanks, experimental wine samples were collected for chemical analysis. The sugar values were determined using a digital refractometer (Atago PAL-87S, Atago USA, Bellevue, WA, USA). The must and wine samples (200 mL) of each treatment (six replicates) were used to determine the pH, volatile acidity (VA), titratable acidity (TA), alcohol volume (AV), and tartaric acid content (TAD). The pH was determined using a pH Pro2Go meter with an InPro X1 Sensor (Mettler-Toledo Co, Columbus, OH, USA). For VA and TA determination, a DS Titra analyzer and Vola 2000 extractor were used (Dujardin-Salleron, Noizay, France). The alcohol content was determined using a DS Ebuliometer with a DS Thermometer (Dujardin-Salleron, Noizay, France). The N content was determined using a Thermo Scientific Orion Star containing a High-performance ammonia electrode (Thermo Fisher Scientific, Walthan, MA, USA).

2.4. Statistical Analysis

Statistical analyses were performed using Graph Pad Prism 8.3 software (GraphPad Software, San Diego, CA, USA). The results of each variable are expressed as mean and standard deviation (SD). One-way analysis of variance (ANOVA) was used to evaluate the statistical significance of the soil and leaf treatment using Duncan's multiple range test (DMRT) between the control and experimental groups during blooming and veraison in leaves. For grapes, wine and must chemical analyses were performed using Student's *t*-test, with a significance level set at $p < 0.05$.

3. Results

The changes in the mineral content of control and experimental groups measured during grape formation are presented in Table 2. At the onset of the experiment, each individual mineral compound present in the soil was measured. The soil of the monitored region was then altered by adding a conventional NPK fertilizer together with minerals (Zn, Ca, Mg, Cu, B, and Fe). In comparison to the initial values, a statistical ($p < 0.05$) increase in these particular minerals in the soil was observed. The vineyard had chlorosis, which made the leveling of minerals particularly important. A long-abandoned section of the vineyard was designated as the experimental area. In order to better monitor the effects of the leaf fertilizer, a designated area was selected. The leaf samples throughout the allotted time were collected for the laboratory analyses. The subsequent application of the leaf fertilizer statistically significantly increased ($p < 0.05$) the monitored mineral compounds of the experimental group. The soil investigation was set up to compare the soil loss of minerals after the grapes were harvested. It was evident that foliar fertilizer application maintained higher values (N, P, K, and Fe). On the other hand, Ca and B mineral levels were significantly ($p < 0.05$) lower than in the control group.

Table 2. The soil mineral content before harvest and post-harvest using standard fertilization and leaf fertilization methods in the Eastern Slovak wine region.

	Soil Measurement Spring 2021	Soil After Standard Fertilization	Leaves from the Control Group After Standard Fertilization	Leaves from the Experimental Group After Standard Fertilization	Leaves from the Experimental Group After Leaf Fertilization	Post-Harvest Soil Control Group
N (kg/ha)	116.59 ± 12.19 ^{b}	170.75 ± 11.71 ^{a}	128.98 ± 8.11 ^{c}	127.05 ± 7.56 ^{c}	131.29 ± 6.54 ^{c}	118.44 ± 8.48 ^{b}
P (mg/kg)	86.46 ± 3.96 ^{b}	116.24 ± 4.93 ^{a}	106.56 ± 1.77 ^{c}	106.86 ± 2.38 ^{c}	109.24 ± 1.96 ^{c}	95.86 ± 1.28 ^{b}
K (mg/kg)	124.59 ± 3.98 ^{b}	280.96 ± 6.05 ^{a}	181.14 ± 1.94 ^{c}	182.24 ± 2.47 ^{c}	192.54 ± 3.42 ^{c}	141.17 ± 2.82 ^{d}
Ca (mg/kg)	1012.64 ± 3.34 ^{b}	2653.88 ± 24.79 ^{a}	1662.29 ± 13.29 ^{c}	1678.98 ± 6.58 ^{c}	1724.21 ± 2.54 ^{c}	2295.25 ± 23.79 ^{a}
Mg (mg/kg)	97.95 ± 0.27 ^{b}	250.95 ± 1.83 ^{a}	158.07 ± 6.38 ^{c}	159.01 ± 5.54 ^{c}	174.84 ± 1.95 ^{d}	135.25 ± 1.92 ^{c}
Fe (mg/kg)	6.25 ± 0.19	7.53 ± 0.06 ^{b}	6.53 ± 0.04	6.47 ± 1.56	7.02 ± 1.53 ^{b}	5.25 ± 0.02 ^{a}
Cu (mg/kg)	0.95 ± 0.04 ^{b}	2.47 ± 0.15 ^{a}	2.40 ± 0.01 ^{a}	2.12 ± 0.01 ^{a}	2.34 ± 0.02 ^{a}	1.78 ± 0.01 ^{c}
Zn (mg/kg)	1.11 ± 0.02 ^{b}	1.71 ± 0.12	1.69 ± 0.01	1.72 ± 0.01	1.91 ± 0.02 ^{a}	1.41 ± 0.01 ^{b}
B (mg/kg)	0.64 ± 0.02 ^{b}	0.91 ± 0.10 ^{b}	1.12 ± 0.02 ^{b}	1.95 ± 0.01 ^{c}	2.34 ± 0.01 ^{a}	0.99 ± 0.02 ^{b}
pH	5.98 ± 0.01	6.32 ± 0.04	6.33 ± 0.01	6.34 ± 0.01	6.41 ± 0.01	6.09 ± 0.01
OM (%)	2.55 ± 0.02 ^{a}	2.64 ± 0.06 ^{a}	2.65 ± 0.08 ^{a}	1.84 ± 0.05 ^{b}	1.91 ± 0.02 ^{b}	1.27 ± 0.01 ^{c}

OM—organic matter. The means with different superscript letters ($^{a, b, c, d}$) in the columns are statistically significantly different in individual parameters (DMRT, $p < 0.05$).

Table 3 shows the mineral content of the foliage. The experimental and control vineyards' leaves were collected diagonally. Leaves were gathered both after the veraison and prior to blooming. The foliar fertilizer was administered at the precise times specified by the manufacturer. Based on the determination of the exact composition of the mineral profile after the application of foliar fertilizer, it was possible to monitor the amount of minerals present in the leaves. During blooming, the experimental sample contents of Ca, P, K, Cu, and B were increased significantly ($p < 0.05$). Following veraison, statistically significant ($p < 0.05$) increases in Ca, P, K, Mg, K, and B concentrations were observed. The concentration of Ca reached a level of 90.45 ± 0.79 mg/kg in the experimental group during blossoming (70.41 ± 1.89 mg/kg in the control group). At the same time, an increase in the Ca content in the leaves during the veraison period was observed in the experimental group (139.76 ± 4.35 mg/kg). Also, a statistically significant increase in Ca content in the leaves with a maximum of 139.76 ± 4.35 mg/kg in the experimental group was measured compared to the control (110.18 ± 1.72 mg/kg). Therefore, by using the foliar fertilizer, higher values than in the control group (110.18 ± 1.72 mg/kg) were achieved. The levels of P in the leaves reached the highest values in the experimental group during the blooming period afterward; however, during the veraison, there was a statistically significant ($p < 0.05$) decrease in P levels in the experimental group up to a value of 90.22 ± 1.52 mg/kg (114.80 ± 1.20 mg/kg in the control group). The K values ranged in approximately the same levels for both monitored groups during the blooming and veraison periods. Statistically significant differences ($p < 0.05$) were observed in the levels of Mg and Zn during the veraison period in the experimental group. The Cu content in the experimental group was statistically significant ($p < 0.05$) in the blooming period. The B content values were statistically significant in the experimental group both in the blooming and veraison periods. During the veraison period, the experimental group (31.12 ± 1.23 mg/kg) achieved the highest values by using a foliar fertilizer with a B compared to the control group (28.86 ± 1.02 mg/kg).

Table 3. The mineral content of leaves before blooming and after veraison (mean ± SD; mg/kg) measured in separate groups after foliar fertilization.

	Blooming		**Veraison**	
	Control	**Experimental**	**Control**	**Experimental**
Ca	70.41 ± 1.89 ^{b}	90.45 ± 0.79 ^{a}	110.18 ± 1.72 ^{b}	139.76 ± 4.35 ^{a}
P	165.25 ± 1.63 ^{b}	262.82 ± 13.52 ^{a}	114.80 ± 1.20 ^{a}	90.22 ± 1.52 ^{b}
K	659.87 ± 14.78 ^{b}	785.42 ± 13.22 ^{a}	569.90 ± 13.82 ^{b}	643.91 ± 5.08 ^{a}
Mg	101.42 ± 2.06	103.64 ± 2.44	91.24 ± 2.60 ^{b}	98.95 ± 1.74 ^{a}
Fe	69.21 ± 6.85	62.28 ± 2.81	77.08 ± 8.68	71.26 ± 4.95
Zn	52.27 ± 0.73	53.36 ± 1.80	42.59 ± 1.93 ^{b}	49.78 ± 1.29 ^{a}
Cu	5.93 ± 0.05 ^{b}	6.19 ± 0.14 ^{a}	8.38 ± 0.35	8.32 ± 1.17
B	25.13 ± 0.82 ^{b}	27.66 ± 0.49 ^{a}	28.86 ± 1.02b ^{a}	31.12 ± 1.23 ^{a}

The means with different superscript letters ($^{a,\,b}$) in the columns for the control and experimental groups during blooming and veraison separately are statistically significantly different in individual parameters (DMRT, $p < 0.05$).

Monitoring of the mineral content was also the aim of the study. To confirm the effect of foliar fertilizer, the amounts of minerals in grape, must, and wine samples were also monitored (Table 4). The amount of Ca in the grapes of the experimental group was significantly higher (96.20 ± 2.34 mg/kg) than in the control group (79.91 ± 1.86 mg/kg). No significance in the must was observed; however, in the case of wine samples, Ca reached a significantly higher concentration in the control sample (86.02 ± 0.52 mg/kg) than in the experimental samples (82.86 ± 0.29 mg/kg). The concentration of P had a decreasing trend in all samples. Statistical differences ($p < 0.05$) between the control and experimental groups for this mineral were observed. The amount of K was higher in the experimental group (672.92 ± 25.30 mg/kg) grapes compared to the control group (519.87 ± 1.72 mg/kg). The amount of K in the must was reduced by half in both groups. The reduction in K in the wine was much higher in the experimental sample (284.08 ± 0.44 mg/kg) than in the control group (238.85 ± 0.24 mg/kg). The measurements of Mg and Fe concentrations in the grape, must, and wine samples did not show any statistically significant differences ($p > 0.05$). The experimental must sample (5.02 ± 0.14 mg/kg) showed a higher amount of Zn compared to the control group (4.02 ± 0.03 mg/kg). Despite the use of a foliar fertilizer containing B, a noticeably lower amount in the grape samples of the experimental group (14.36 ± 2.35 mg/kg) compared to the control group (18.13 ± 0.70 mg/kg) was recorded. However, after pressing the berries, the levels of B in the must (0.71 ± 0.06 mg/kg) and, subsequently, in the wine (0.61 ± 0.06 mg/kg) were significantly ($p < 0.05$) higher in the experimental group.

Table 4. The mineral content of the control and experimental groups of grapes, must, and wine.

(mg/kg)	**Grapes**		**Must**		**Wine**	
	Control	**Experimental**	**Control**	**Experimental**	**Control**	**Experimental**
Ca	79.91 ± 1.86 ^{b}	96.20 ± 2.34 ^{a}	94.97 ± 1.34	94.21 ± 4.54	86.02 ± 0.52 ^{a}	82.86 ± 0.29 ^{b}
P	155.05 ± 1.63 ^{b}	215.32 ± 2.12 ^{a}	152.39 ± 2.39 ^{b}	173.18 ± 3.52 ^{a}	149.34 ± 0.37 ^{b}	161.77 ± 0.49 ^{a}
K	519.87 ± 1.72 ^{b}	672.92 ± 25.30 ^{a}	274.09 ± 11.97 ^{b}	321.46 ± 4.47 ^{a}	238.85 ± 0.24 ^{b}	284.08 ± 0.44 ^{a}
Mg	93.92 ± 3.28	95.14 ± 1.70	85.45 ± 1.05	85.77 ± 3.19	74.81 ± 0.18	74.35 ± 0.33
Fe	64.41 ± 1.49	62.03 ± 1.70	5.89 ± 0.43	5.67 ± 0.21	5.33 ± 0.07	5.23 ± 0.08
Zn	72.27 ± 0.73	68.36 ± 4.95	4.02 ± 0.03 ^{b}	5.02 ± 0.14 ^{a}	3.76 ± 0.19	3.83 ± 0.12
Cu	6.68 ± 0.45	6.61 ± 0.36	3.42 ± 0.05	3.48 ± 0.09	0.37 ± 0.01	0.38 ± 0.01
B	18.13 ± 0.70 ^{a}	14.36 ± 2.35 ^{b}	0.38 ± 0.02 ^{b}	0.71 ± 0.06 ^{a}	0.36 ± 0.01 ^{b}	0.61 ± 0.06 ^{a}

The means with different superscript letters ($^{a,\,b}$) in the columns are statistically significantly different in individual parameters (DMRT, $p < 0.05$).

The grape yield parameters and grape quality parameters were measured (Figures 1 and 2). The harvest yield was 2.78 ± 0.02 kg/plant for the control group. A significantly ($p < 0.05$)

lower harvest yield was present in the experimental group (2.69 ± 0.03 kg/plant). The titratable acidity, sugar, and pH values were measured in both groups using juice from 100 freshly pressed berries collected from the vineyard using a standard sampling method. Statistically significant ($p < 0.05$) acidity was observed in the control (11.56 ± 0.04 g/L) compared to the experimental group (11.28 ± 0.03 g/L). The value of sugar in the control group (21.69 ± 0.02 °Brix) was significantly ($p < 0.05$) higher than in the experimental group samples (20.97 ± 0.03 °Brix).

The must and wine chemical composition results are shown in Table 5. Despite the fact that both samples underwent an identical process using the same technology, statistically significant ($p < 0.05$) changes were observed. The use of the foliar fertilizer significantly ($p < 0.05$) affected the TA of the experimental group (11.73 ± 0.20 g/L). Lower amounts of acid in the must affected the pH values, resulting in a lower pH value in the control group (3.21 ± 0.01) compared to the experimental group (3.23 ± 0.01). The concentration of N compounds was significantly higher in the experimental group (176.24 mg/L). Regarding the produced control and experimental wine samples, the pH values were also affected. The control group had lower values (3.16 ± 0.01) compared to the experimental group (3.21 ± 0.02). Although the sugar content was not significantly changed ($p > 0.05$), the alcohol volume was higher in the control group (12.82 ± 0.05%). The same results were observed for the TAD levels (2.31 ± 0.02 g/L) in the control group samples.

Table 5. The chemical parameters of the produced must and wine.

Must	Sugar (g/L)	TA (g/L)	pH	NC (mg/L)
Control	22.12 ± 0.47	11.98 ± 0.16 ^{a}	3.21 ± 0.01 ^{b}	168.36 ± 0.01 ^{b}
Experimental	21.52 ± 0.77	11.73 ± 0.20 ^{b}	3.23 ± 0.01 ^{a}	176.24 ± 0.02 ^{a}

Wine	pH	AV (%)	Sugar (g/L)	TA (g/L)	VA (g/L)	TAD (g/L)
Control	3.16 ± 0.01 ^{b}	12.82 ± 0.05 ^{a}	4.02 ± 0.04	7.45 ± 0.04	0.82 ± 0.02	2.31 ± 0.02 ^{a}
Experimental	3.21 ± 0.02 ^{a}	12.71 ± 0.03 ^{b}	4.27 ± 0.01	7.47 ± 0.02	0.79 ± 0.07	2.26 ± 0.05b ^{a}

VA—volatile acidity, TA—titratable acidity, AV—alcohol volume, TAD—tartaric acid, NC—nitrogen compounds; ^{a,b}—values in all the columns are statistically significant (Student's *t*-test, $p < 0.05$).

4. Discussion

Fertilizers with varying NPK levels and micronutrients are used all over the world to increase grape yield and quality. A lack of mineral nutrients causes chlorosis and, eventually, leaf necrosis, affecting grape quality in terms of sugar and polyphenol content as well as vine growth and output. On the other hand, giving grapevines mineral nutrients could alter the physicochemical makeup of the fruit and its byproducts. Therefore, it is crucial to use both organic and inorganic fertilizers in an integrated way to boost productivity, enhance grape quality, and guarantee sustainable production [10,24–26]. Limits for metals and minerals do not exist. However, many countries have set maximum permissible levels of certain metals and minerals in wine, considering both their enological and toxicological effects [27,28]. The International Organization of Vine and Wine (OIV) also prescribes the permitted levels of metals and minerals in wine [27]. The natural levels of trace elements in wine are typically non-toxic. Agricultural practices can change the composition of trace elements via the use of various fertilizers and pesticides [3,29,30].

Following the application of the leaf fertilizer presented in this study, a statistically significant increase ($p < 0.05$) in the monitored mineral compounds of the experimental group was observed. At the beginning of the experiment, the NPK values in the control and experimental group leaves were, in terms of average values, very similar ($p > 0.05$). The application of the used commercial foliar fertilizer product in the experimental group increased the concentration of NPK. This is an expected phenomenon since nutrients are absorbed through the leaves. Aljabary et al. [13] also demonstrated that the leaf surface absorbs nutrients better after HA was added to foliar fertilizer. This had a direct impact on berry yield [31]. This theory was also confirmed by our study when, similarly, the experimental group had higher values for cluster weight (201.38 ± 1.01 g), berry weight (192.87 ± 1.09 g), and berry volume (134.49 ± 1.791 mL) compared to the control group (cluster weight: 199.04 ± 1.01 g; berry weight: 187.22 ± 0.57 g; berry volume: 129.19 ± 1.13 mL).

At the same time, there was also an increase in the amount of K (181.14 ± 1.94 mg/kg in the control group) in the leaves of the experimental group (192.54 ± 3.42 mg/kg). Foliar fertilizers are frequently utilized as a soil fertilizer substitute since it is challenging to raise subsoil K concentrations in an existing vineyard [31,32]. Our experimental findings suggest that foliar K administration is most likely insufficient to provide a grapevine supply of K. The foliar fertilizers affected the content of K in grapevine leaves in the observed period. The high mobility of K in plants could be one reason [33]. There are two possible explanations for these results. First, according to the results of foliar analysis, K fertilizers could not increase the K concentration of grapevines; therefore, they could not lessen the occurrence of grape wilting. The deficiency of K is not the main cause of the occurrence of grape wilting, as had been proposed earlier [34].

Measurements of mineral content during the blooming and veraison periods confirmed the accumulation of minerals in the leaves of the experimental group. The P (262.82 ± 13.52 mg/kg) and K (785.42 ± 13.22 mg/kg) concentrations were significantly higher in the experimental group during the blooming period compared to control samples (P-165.25 ± 1.63 mg/kg and K-659.87 ± 14.78 mg/kg). After veraison, P 114.80 ± 1.20 mg/kg in the control group) concentrations significantly decreased in the experimental group (90.22 ± 1.52 mg/kg). Usually, when the P concentration is higher in the soil, it is higher in the leaves as well [24,32]. Consequently, in P-deficient soils, yield components such as the number and weight of clusters and berries increase with P addition [35]. The results of these studies are not in agreement with our results. As Figure 2 shows, the experimental group had higher berry and cluster quality. Our results are supported by the study by Stefanello et al. [36].

The application of B throughout foliar fertilizer can be a beneficial and ecological technique. Supplementation of B in the plant can increase the absorption and transport of minerals in different parts of the plant, improving agricultural production [37]. The presence of B in the wine is adequate in terms of concentrations in the soil, and it is fundamental for the flowering and fruiting process. Low concentrations or the absence of boron is one of the most common deficiencies in the grapevine and causes a significant loss of grape quality [37–40]. The foliar application provides greater uniformity in terms of micronutrient distribution in plants. Its use has a short duration and must be applied in specific growth periods [40–43]. The concentration of B in the experimental group was higher during blooming (27.66 ± 0.49 mg/kg) and veraison (31.12 ± 1.23 mg/kg) periods compared to the control samples (25.13 ± 0.82 mg/kg—blooming; 28.86 ± 1.02 mg/kg—veraison). Since B has a positive effect on the intensity of photosynthesis, sugar content in grapes, and reducing inflorescence shedding and differentiation of inflorescences into buds, the results of grape yield and quality parameters (Figures 1 and 2) support our conclusion that the addition of B in foliar fertilizer has a positive effect on growth and production.

Minerals also change the wine extract, which plays a role in the creation of the taste, aroma, freshness, overall impression, and chemical composition [42,43]. Specific concentrations of Ca, K, Mg, and Na are important for cellular metabolism and successful must fermentation [14,44]. Therefore, the effect of foliar fertilization on the transition between must and wine was monitored. The main macro elements and a few trace elements (K, P, Mg, B, Fe, and Cu) accumulate in grape berries gradually during their development, with the greatest accumulation occurring after the locking of berries [8,13,15,44,45].

The transfer of the minerals from leaves to grapes and subsequently to the wine was observed. In the experimental group, the concentration of Ca was statistically higher in the wine and fruit. The values in must were equivalent. The values of P in the experimental group were higher than in the control group grapes, must, and wine, even though there was less P accumulation during veraison. The concentration of K in the experimental group was statistically increased ($p < 0.005$). Grapes had the highest concentration, which dropped during processing (284.08 ± 0.44 mg/kg) compared to the control group (238.85 ± 0.24 mg/kg). Grapes are the main recipient of K after locking, which is mainly transported via the leaves, roots, and older wood. Due to the leaf fertilization method, higher concentrations of K accumulated in the grape berries and, therefore, in the wine [13,31,32,45,46]. At the same time, K changes the pH of musts, which can be dangerous for freshly produced wine musts. High amounts of K also reduce the content of acids [31]. Excessive quantities of K, Ca, Fe, and Cu contribute to the cloudiness of wine and/or they precipitate as tartrates in wine. The Ca concentrations range from 0.5 to 2 g/L with an average of 1 g/L. The highest K levels were usually found in wine made from grapes concentrated via noble rot. [45–47]. Peršurič et al. [31] studied the addition of K in a vineyard with a low K concentration in the soil. Their results showed a positive effect of foliar fertilization. Control treatment (1.53% of K) was affected positively. Other treatments (0.8–0.96%) used in their study were within the optimal range [48]. The concentration of Mg in the leaves of their experimental groups was lower than the ideal range. A study by Garcia-Escudero et al. [48] showed a clear antagonistic relationship between K and Mg. Nevertheless, Peršurič et al. [31] demonstrated that treatment can change the ratio of K/Mg.

Traces of Zn are naturally present in must and wine [4]. Significantly increased levels of Zn (5.02 ± 0.14) in the experimental group were observed in must samples. The levels of B were higher in the experimental group, which supports the theory of the transition from leaves to grapes. Due to the solubility of all Mg salts, the experimental wine had a higher concentration of Mg (74.35 ± 0.33 mg/kg) than the control (74.81 ± 0.18 mg/kg) wine samples. However, the concentrations of Mg were not significantly affected by leaf fertilization. According to Plotka-Wasylka et al. [49], there is a notable association between the mineral concentrations in the eastern and middle regions of Europe. The K level interval matched those of the French wines that were reported. In comparison to the results of experimental wine in French, Italian, Polish, and Czech wines, we found that our K levels were comparable. The Ca concentration was higher than in the wine samples from the Czech, French, Italian, and Spanish studies that were presented. As seen in the study of Shimizu et al. [9], the winemaking method changed the mineral concentrations in the wine. However, the mineral scores varied in all the samples of wine as a result of the use of various types of grapes for the measurements. According to these findings, the effects on the mineral composition of wine are minimal in comparison to the variations due to the utilization of different types of grapes [48,50–59]. The study by Blotevogel et al. [54] showed that Mg accumulates in grape seeds. Winemaking techniques such as the maceration of grapes can improve the concentration of minerals [7,54–60].

The quality of produced must and wine was significantly changed, mainly in the measurement of Ta, pH, and NC in must. The produced wine showed changes in pH, AV, and TAD measurements. Several studies showed that the application of foliar fertilizer increased the content of sugars in must [31]. Our results showed that the sugar content was lower in the experimental group (21.52 ± 0.77 g/L). Lošák et al. [55] changed the K concentration in leaves, which resulted in a change in sugar values in the must. Similar changes were also observed by Peršurič et al. [31,32]. However, these results contradict the result that low K levels lead to a decrease in sugar concentration. Statistically significant differences in sugar concentration were not observed in the experimental group. However, the concentration of K was higher in the experimental group, despite the fact that the must had a lower sugar concentration. According to the results, this theory was not confirmed. In previous research by Peršurič et al. [32], treatments with Mg and P significantly affected the sugar content within optimal values. According to studies by Daudt [56] and Dequin et al. [57], sugar accumulation depends not only on the supply of minerals but also on the weather. The amount of precipitation and sunlight directly affects the storage of sugars in grapes. However, mineral supplementation promotes an increase in the accumulation of sugars in grapes. The results of sugar content presented in this study support the effect of climate conditions when the sugar concentration in the control group (21.69 ± 0.02 °Brix) was significantly ($p < 0.05$) higher than in the experimental group samples (20.97 ± 0.03 °Brix). Despite the fact that both groups had the same climatic conditions, foliar fertilization with added K did not show an increase in sugar levels. These results were supported by the study by Peršurič et al. [32].

Fertilizers containing biostimulants such as humic acids can improve the uptake and efficiency of nutrient utilization [13,28,29,44,50]. The most important factors determining the mineral content in wine include the soil on which vineyards are located, the capacity of grapes to take up various minerals, the production cycle, and the maturation techniques [58–60].

5. Conclusions

It can be concluded that the application of a foliar fertilizer with HA and B affected the overall mineral profile of the examined wine samples. The addition of a commercial product in an amount of 0.5 L/hL and the impact on the mineral profile of the leaves, yield, and quality of produced grapes per hectare of the cultivated area was studied. After the application of the commercial product, a statistically significant change in the mineral profile of the leaves was detected. A statistically significant ($p < 0.005$) increase in N, P, K, Ca, Mg, Zn, and B concentrations was observed in the leaves from the experimental group. Concentrations of selected minerals were affected during the blooming and veraison period.

The affected mineral content observed in grapes, must, and wine was predominantly Ca, P, K, Zn, and B concentrations. The qualities of grapes and berries were identified as significantly improved in the experimental group. Nevertheless, the total acid and sugar concentration values were higher in the control group. However, further studies are necessary to determine the optimal concentration of foliar fertilizer with regard to a reduction in important mineral components such as Zn, P, K, and B. The foliar fertilizer used in this study influenced the mineral concentration of the leaves, grapes, and final wine. The concentrations of P, K, and B in all experimental samples were significantly influenced. Therefore, it can be concluded that HA and B affected the transfer of minerals from leaves and soil to the produced wine samples.

Author Contributions: Conceptualization, M.B., V.B., I.R. and S.M.; methodology, M.B., B.S. and S.M.; software, M.B.; validation, M.B. and B.S.; formal analysis, M.B., P.O. and L.Š.; investigation, M.B.; resources M.B.; data curation, B.S. and M.B.; writing—original draft preparation, M.B.; writing—review and editing, M.B. and B.S.; visualization, M.B.; supervision, M.B. and V.B.; project administration, B.S.; funding acquisition, B.S. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the Science Grant Agency of the Ministry of Education, Science, Research and Sport of the Slovak Republic and the Slovak Academy of Sciences under the project VEGA 1/0156/21.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available within the article.

Acknowledgments: We would like to thank Leah Eleanor Browne and Serena Faith Amrit for proofreading and editing the English language.

Conflicts of Interest: The authors declare no conflicts of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

References

1. Ciampa, A.; Dell'Abate, M.T.; Florio, A.; Tarricone, L.; Di Gennaro, D.; Picone, G.; Trimigno, A.; Capozzi, F.; Benedetti, A. Combined magnetic resonance imaging and high resolution spectroscopy approaches to study the fertilization on metabolome, morphology and yeast community of wine grape berries, cultivar *Nero di Troia*. *Food Chem.* **2019**, *274*, 831–839. [CrossRef]
2. Cataldo, E.; Fucile, M.; Mattii, G.B. Biostimulants in Viticulture: A sustainable approach against biotic and abiotic Stresses. *Plants* **2022**, *11*, 162. [CrossRef]

3. Webb, L.; Whetton, P.H.; Barlow, E.W.R. Modelled impact of future climate change on the phenology of winegrapes in Australia. *Aust. J. Grape Wine Res.* **2007**, *13*, 165–175. [CrossRef]
4. Potort, A.G.; Turco, V.L.; Saitta, M.; Bua, G.D.; Tropea, A.; Dugo, G.; Di Bella, G. Chemometric analysis of minerals and trace elements in Sicilian wines from two different grape cultivars. *Nat. Prod. Res.* **2017**, *31*, 1000–1005. [CrossRef]
5. Moreno, J.; Peinado, R. *Enological Chemistry*, 1st ed.; Academic Press Inc.: Madrid, Spain, 2012; pp. 1–442.
6. Canellas, L.P.; Olivares, F.L.; Aguiar, N.O.; Jones, D.L.; Nebbioso, A.; Mazzei, P.; Piccolo, A. Humic and fulvic acids as biostimulants in horticulture. *Sci. Hortic.* **2015**, *196*, 15–27. [CrossRef]
7. Ribéreau-Gayon, P.; Glories, Y.; Maujean, A.; Dubourdieu, D. *Handbook of Enology: The Chemistry of Wine Stabilization and Treatments*, 2nd ed.; John Wiley & Sons Inc.: Hoboken, NJ, USA, 2006; Volume 2, pp. 1–441.
8. Almeida, C.M.R.; Vasconcelos, M.T.S.D. Multielement composition of wines and their precursors including provenance soil and their potentialities as fingerprints of wine origin. *J. Agric. Food Chem.* **2003**, *51*, 4788–4798. [CrossRef] [PubMed]
9. Shimizu, H.; Akamatsu, F.; Kamada, A.; Koyama, K.; Iwashita, K.; Goto-Yamamoto, N. Variation in the mineral composition of wine produced using different winemaking techniques. *J. Biosci. Bioeng.* **2020**, *130*, 166–172. [CrossRef]
10. Ferrara, G.; Brunetti, G. Effects of the times of application of a soil humic acid on berry quality of table grapes (*Vitis vinifera* L.) cv Italia. *Span. J. Agric. Res.* **2010**, *8*, 817–822. [CrossRef]
11. Islam, M.A.; Morton, D.W.; Johnson, B.B.; Angove, M.J. Adsorption of humic and fulvic acids onto a range of adsorbents in aqueous systems, and their effect on the adsorption of other species: A review. *Sep. Purif. Technol.* **2020**, *247*, 116949. [CrossRef]
12. Abd EL-Rahman, M.M.A.; Khodair, O.A.; Hamed, M.H. Impact of organic bio fertilization and humic acid on growth and fruiting on flame seedles grapevines under sandy soil conditions. *J. Plant Prod.* **2021**, *12*, 171–177.
13. Aljabary, A.M.O.; Al-Baytie, M.R.S.; Ahmed, Z.S. Effect of number eyes left after pruning, fertilization with humic acid and spraying with gibberellic acid in some mineral content of vineyards thompson cv. *Vitis vinifera* L. *Plant Arch.* **2018**, *18*, 2061–2067.
14. Lasa, B.; Menendez, S.; Sagastizabal, K.; Cervantes, M.E.; Irigoyen, I.; Muro, J.; Aparicio-Tejo, P.M.; Ariz, I. Foliar application of urea to Sauvignon blanc and Merlot vines: Doses and time application. *Plant Growth Regul.* **2012**, *67*, 73–81. [CrossRef]
15. Popescu, G.C.; Popescu, M. Yield, berry quality and physiological response of grapevine to foliar humic acid application. *Bragantia Camp.* **2018**, *77*, 273–282. [CrossRef]
16. Asgharzade, A.; Babaeian, M. Investigating the effects of humic acid and acetic acid foliar application on yield and leaves nutrient content of grape (*Vitis vinifera*). *Afr. J. Microbiol. Res.* **2012**, *6*, 6049–6054. [CrossRef]
17. Derrien, M.; Lee, Y.K.; Park, J.E.; Li, P.; Chen, M.; Lee, S.H.; Lee, S.H.; Lee, J.B.; Hur, J. Spectroscopic and molecular characterization of humic substances (HS) from soils and sediments in a watershed: Comparative study of HS chemical fractions and the origins. *Environ. Sci. Pollut. Res.* **2017**, *24*, 16933–16945. [CrossRef] [PubMed]
18. El-Boray, M.S.; Mostafa, M.F.; Shaltout, A.D.; Hassan, K.H. Influence of fulvic acid plus some microelements and microorganisms on yield and quality characteristics of Superior Seedles grapevines. *J. Plant Prod.* **2015**, *6*, 287–305.
19. Abdel-Fattah, M.E.S.; Moamen, M.A.W.; El-Nopy, H.S.; Osama, G.E.M.A. Minimizing mineral N Fertilization Superior Seedless Grapevines by Using Humic and Fulvic acids. *Assiut J. Agric. Sci.* **2023**, *54*, 227–238.
20. Eman, A.A.; Abd El-Monem, M.; Saleh, R.M.; Mostafa, E.A.M. Minimizing the quantity of mineral nitrogen fertilizers on grapevine by using humic acid, organic and bio fertilizers. *Res. J. Agric. Biol. Sci.* **2008**, *4*, 46–50.
21. Horneck, D.A.; Miller, R.O. Determination of total nitrogen in plant tissue. In *Handbook of Reference Methods for Plant Analysis*; CRC Press: Boca Raton, FL, USA, 1998; pp. 75–83.
22. Pérez-Álvarez, E.P.; García, R.; Barrulas, P.; Dias, C.; Cabrita, M.J.; Garde-Cerdán, T. Classification of wines according to several factors by ICP-MS multielement analysis. *Food Chem.* **2019**, *270*, 273–280. [CrossRef] [PubMed]
23. Asendorf, S. *Thermo Fisher Scientific Application Note 44392.: Analysis of Infant Formulae and Milk Powders Using the Thermo Scientific iCAP 7400 ICP-OES Duo*; Thermo Fisher Scientific: Waltham, MA, USA, 2018.
24. Ciotta, M.N.; Ceretta, C.A.; Ferreira, P.A.; Stefanello, L.O.; Couto, R.R.; Tassianri, A.; Marchezan, C.; Girotto, E.; de Conti, L.; Lourenzi, C.R.; et al. Phosphorus fertilization for young grapevines of Chardonnay and Pinot Noir in sandy soil. *Idesia* **2018**, *36*, 27–34. [CrossRef]
25. Greenough, J.D.; Lengerich, H.P.; Jackson, S.E. Element fingerprinting of Okanagan Valley wines using ICP-MS: Relationships between wine composition, vineyard and wine colour. *Aust. J. Grape Wine Res.* **1997**, *3*, 75–83. [CrossRef]
26. James, A.; Mahinda, A.; Mwamahonje, A.; Rweyemamu, E.W.; Mrena, E.; Aloys, K.; Massawe, C. A review on the influence of fertilizers application on grape yield and quality in tropics. *J. Plant Nutr.* **2022**, *46*, 2936–2957. [CrossRef]
27. Available online: https://www.oiv.int/standards/international-code-of-oenological-practices/annexes/maximum-acceptable-limits (accessed on 12 November 2024).
28. Yang, Y.; Duan, C.; Du, H.; Tian, J.; Pan, Q. Trace elements and rare earth element profiles in berry tissues of three grape cultivars. *Am. J. Enol. Vitic.* **2010**, *61*, 401–407. [CrossRef]
29. Minoia, C.; Sabbioni, E.; Ronchi, A.; Gatti, A.; Pietra, R.; Nicolotti, A.; Fortaner, S.; Balducci, C.; Fonte, A.; Roggi, C. Trace element reference values in tissues from inhabitants of the European Community. *Sci. Total Environ.* **1994**, *141*, 181–195. [CrossRef]
30. Stafilov, T.; Karadjova, I. Atomic absorption spectrometry in wine analysis—A review. *Maced. J. Chem. Chem. Eng.* **2009**, *28*, 17–31. [CrossRef]
31. Peršurić Palčić, A.; Jeromel, A.; Pecina, M.; Palčić, I.; Gluhić, D.; Petek, M.; Herak Ćustić, M. Decreased Leaf Potassium Content Affects the Chemical Composition of Must for Sparkling Wine Production. *Horticulturae* **2022**, *8*, 512. [CrossRef]

32. Peršurić Palčić, A.; Jeromel, A.; Pecina, M.; Palčić, I.; Gluhić, D.; Herak Ćustić, M. Effect of foliar fertilization on cv. Istrian Malvasia (*Vitis vinifera* L.) must on basic chemical composition. *Glas. Zašt. Bilja* **2020**, *4*, 32–38. [CrossRef]
33. Marschner, H. *Mineral Nutrition of Higher Plants*, 2nd ed.; Academic Press: London, UK, 2002.
34. Fardossi, A. Aspekte der Rabenährung (Aspects of Grapevine Nutrition). *Der Winz.* **2001**, *57*, 6–13.
35. Schmitt, D.E.; Borghezan, M.; Ambrosini, V.G.; Comin, J.J. Yield and must composition of grapevines subjected to phosphate fertilization in Southern Brasil. *Pesqui. Agropecu. Bras.* **2020**, *55*, 11–67. [CrossRef]
36. Stefanello, L.; Schwalbert, R.; Schwalbert, R.; Tassinari, A.; Garlet, L.; De Conti, L.; Ciotta, M.; Ceretta, C.; Ciampitti, I.; Brunetto, G. Phosphorus critical levels in soil and grapevine leaves for South Brazil vineyards: A Bayesian approach. *Eur. J. Agron.* **2023**, *144*, 126752. [CrossRef]
37. Kostič, D.; Mitič, S.; Miletič, G.; Despotovič, S.; Zarubica, A. The concentrations of Fe, Cu and Zn in selected wines from South-East Serbia. *J. Serbian Chem. Soc.* **2010**, *75*, 1701–1709. [CrossRef]
38. Ali, M.R.; Mehraj, H.; Uddin, A.F.J. Effects of foliar application of zinc and boron on growth and yield of summer tomato. *J. Biosci. Agric. Res.* **2015**, *6*, 512–517. [CrossRef]
39. Gupta, K.; Abhijit, D.; Gupta, B. Plant polyaminases in abiotic stress responses. *Acta Physiol. Plant* **2013**, *35*, 2015–2036. [CrossRef]
40. Cabrita, M.J.; Martins, N.; Barrulas, P.; Garcia, R.; Dias, C.B.; Perez-Alvarez, E.P.; Freitas, A.M.C.; Garde-Cerdán, T. Multi-element composition of red, white and palhete amphora wines from Alentejo. *Food Control* **2018**, *92*, 80–85. [CrossRef]
41. Fernández, V.; Sotiropoulos, T.; Brown, P.H. *Foliar Fertilization: Scientific Principles and Field Practices*; International Fertilizer Industry Association: Paris, France, 2013.
42. Garde-Cedran, T.; López, R.; Portu, J.; González-Arenzana, L.; López-Alfaro, I.; Santamaria, P. Study of the effects of proline phenylalanine and urea foliar application to Tempranillo vineyards on grape amino acid content. Comparison with commercial nitrogen fertilisers. *Food Chem.* **2014**, *163*, 136–141. [CrossRef] [PubMed]
43. Sabit, A.; Yazar, K.; Sabir, F.; Kara, Z.; Yazici, M.A.; Goksu, N. Vine growth, yield, berry quality attributes and leaf nutrient content of grapevines as influenced by seaweed extract (*Ascophyllum nodosum*) and nanosize fertilizer pulverizations. *Sci. Hortic.* **2014**, *175*, 1–8.
44. Catarino, S.; Madeira, M.; Monteiro, F.; Rocha, F.; Curvelo-Garcia, A.S.; De Sousa, R.B. Effect of bentonite characteristics on the elemental composition of wine. *J. Agric. Food Chem.* **2008**, *56*, 158–165. [CrossRef] [PubMed]
45. Akamatsu, F.; Shimizu, H.; Kamada, A.; Igi, Y.; Fujii, T.; Goto-Yamamoto, N. Increase in the oxygen stable isotopic composition of water in wine with low ethanol yield. *Sci. Rep.* **2019**, *9*, 1103. [CrossRef]
46. Dienes-Nagy, Á.; Marti, G.; Breant, L.; Lorenzini, F.; Fuchsmann, P.; Baumgartner, D.; Zufferey, V.; Spring, J.-L.; Gindro, K.; Viret, O.; et al. Identification of putative chemical markers in white wine (Chasselas) related to nitrogen deficiencies in vineyards. *Oeno One* **2020**, *54*, 583–599. [CrossRef]
47. Casassaa, L.F.; Cejaa, G.M.; Vega-Osornoa, A.; Fresne, F.; Llodrac, D. Detailed chemical composition of Cabernet Sauvignon wines aged in French oak barrels coopered with three different stave bending techniques. *Food Chem.* **2021**, *340*, 127573. [CrossRef]
48. García-Escudero, E.; Romero, I.; Benito, A.; Domínguez, N.; Martín, I. Reference Levels for Leaf Nutrient Diagnosis of cv. Tempranillo Grapevine in the Rioja Appellation. *Commun. Soil Sci. Plant Anal.* **2013**, *44*, 645–654. [CrossRef]
49. Plotka-Wasylka, J.; Rutkowska, M.; Cieslik, B.; Tyburcy, A.; Namiesnik, J. Determination of selected metals in fruit wines by spectroscopic techniques. *J. Anal. Methods Chem.* **2017**, *2017*, 5283917. [CrossRef]
50. Niimi, J.; Liland, K.H.; Tomic, O.; Jeffery, D.W.; Bastian, S.E.P.; Boss, P.K. Prediction of wine sensory properties using mid infrared spectra of Cabernet Sauvignon and Chardonnay grape berries and wines. *Food Chem.* **2021**, *344*, 128634. [CrossRef]
51. Rossano, E.C.; Szilágyi, Z.; Malorni, A.; Pocsfalyi, G. Influence of winemaking practices on the concentration of rare earth elements in white wines studied by inductively coupled plasma mass spectrometry. *J. Agric. Food Chem.* **2007**, *55*, 311–317. [CrossRef]
52. Hopfer, H.; Nelson, J.; Collins, T.S.; Heymann, H.; Ebeler, S.E. The combined impact of vineyard origin and processing winery on the elemental profile of red wines. *Food Chem.* **2015**, *172*, 486–496. [CrossRef] [PubMed]
53. Ahmad, I.; Saquib, R.U.; Qasim, M.; Saleem, M.; Khan, A.S.; Yaseen, M. Humic acid and cultivar effects on growth, yield, vase life, and corm characterictics of gladiolus. *Chil. J. Agric. Res.* **2013**, *73*, 339–344. [CrossRef]
54. Blotevogel, S.; Schreck, E.; Laplanche, C.; Besson, P.; Saurin, N.; Audry, S.; Viers, J.; Oliva, P. Soil chemistry and meteorological conditions influence the elemental profiles of Westeuropean wines. *Food Chem.* **2019**, *298*, 125033. [CrossRef]
55. Lošák, T.; Zezulová, T.; Baroň, M.; Elbl, J.; Kintl, A.; Ducsay, L.; Varga, L.; Torma, S.; Petek, M. Foliar application of potassium to grapevine (*Vitis vinifera* L.). *Agrochémia* **2020**, *1*, 23–27.
56. Daudt, C.E.; Fogaça, A. Effect of tartaric acid upon potassium, total acidity and pH, during the vinification of Cabernet Sauvignon grapes. *Ciênc. Rural* **2008**, *38*, 2345–2350. [CrossRef]
57. Dequin, S.; Escudier, J.L.; Bely, M.; Noble, J.; Albertin, W.; Masneuf-Pomarède, I.; Marullo, P.; Salmon, J.M.; Sablayrolles, J.M. How to adapt winemaking practices to modified grape composition under climate change conditions. *Oeno One* **2017**, *51*, 205–214. [CrossRef]
58. Torres, R.L.; De La Fuente Lloreda, M.; Gonzalez, P.J.; Lissarrague García-Gutierrez, J.R.; Baeza Trujillo, P. Effect of soil management strategies on the characteristics of the grapevine root system in irrigated vineyards under semi-arid conditions. *Aust. J. Grape Wine Res.* **2018**, *24*, 439–449. [CrossRef]

59. Thiel, G.; Geisler, G.; Blechschmidt, I.; Danzer, K. Determination of trace elements in wines and classification according to their provenance. *Anal. Bioanal. Chem.* **2004**, *378*, 1630–1636. [CrossRef] [PubMed]
60. Parr, W.V.; Valentin, D.; Breitmeyer, J.; Peyron, D.; Darriet, P.; Sherlock, R.; Robinson, B.; Grose, C.; Ballester, J. Perceived minerality in sauvingon blanc wine: Chemical reality of cultural construct? *Food Res. Int.* **2016**, *87*, 168–179. [CrossRef] [PubMed]