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Impact of Organic Agriculture on the Quality of Grapes (Syrah and Tempranillo) Harvested in Guanajuato, Mexico: Relationship Between Soil Elemental Profile and Grape Bioactive Properties

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Academic Editors: Luigino Barisan and Elisa Giampietri

Received: 19 December 2024
Revised: 10 January 2025
Accepted: 11 January 2025
Published: 14 January 2025

Citation: Macías-Gallardo, F.; Quiñones-Muñoz, T.A.; Miranda-Avilés, R.; Ramírez-Santoyo, L.F.; Zanor, G.A.; Ozuna, C. Impact of Organic Agriculture on the Quality of Grapes (Syrah and Tempranillo) Harvested in Guanajuato, Mexico: Relationship Between Soil Elemental Profile and Grape Bioactive Properties. *Agriculture* **2025**, *15*, 169. https://doi.org/10.3390/agriculture15020169

Abstract: Viticulture has migrated to organic management to reduce environmental impact. Grapes harvested in organic vineyards (ORGs) could have a better polyphenol profile than conventional vineyards (CONs). The objective was to evaluate the relationship between agricultural management, elemental soil profile, and grape bioactive compounds (var. Syrah and Tempranillo). Soil components were determined from CON and ORG vineyards; they were correlated with bioactive compounds in grape skin and seed through principal component analysis (PCA). The ORG vineyard presented higher moisture (4.50–5.72%), clay (31.70–40.55%), organic matter (OM) (9.44–11.01%), P (108.72–122.16 mg/kg), N (0.27 mg/kg), and oxides (Fe_2O_3, SiO_2, MnO, TiO_2) in soil and phenolic compounds (myricetin, quercetin, resveratrol, ellagic acid, others) and antioxidant capacity in grape skin and seed. Regarding PCA (>74.20% of variance), the first component showed positive correlations (>0.60) between pH, moisture, clay, and soil oxides (MgO, K_2O, Al_2O_3), which favored biosynthesis in grape skin and seed phenols (catechin, gallic acid, vanillic acid, and rutin). The second component showed positive correlations between OM, silt, soil oxides, antioxidant capacity, and phenols in grape skin and seed. Finally, the edaphic conditions of the ORG vineyard allowed for one to obtain optimal grapes for winemaking due to their higher phenol content.

Keywords: viticulture; sustainable practices; minerals; grape seed; grape skin; phenolic profile

1. Introduction

Currently, worldwide grape and wine production has had a positive impact on the economy, technology, and science [1,2]. By 2023, the International Organization of Vine and Wine (OIV) indicated that vineyard plantations exceeded 7 million ha globally [3]. Therefore, it is estimated that approximately 281 million tons of grapes will be produced for winemaking during the 2023–2024 period [4]. In this sense, Mexico has 16 states dedicated to grape and wine production, positioning it as the 33rd largest producer in the world [5–7]. In 2023, vineyard plantings were reported to exceed 35,000 ha, resulting in a production of approximately 452,000 tons of grapes [6].

In 2023, the OIV indicated a global decline in wine production of 10% compared with 2022. This trend is attributed to climate change and soil erosion, which have directly affected grape production [8]. In response, winegrowers have started adopting sustainable agricultural management to mitigate their negative impact on the environment [9,10]. In this context, organic agricultural management in viticulture helps reduce the negative impact on biodiversity, minimizes the use of potentially toxic agrochemicals, enhances the control of native yeasts, and promotes a circular economy [11]. However, various authors have mentioned that the implementation of organic practices allows a positive socio-economic impact at the local and regional levels [12]. Additionally, organic agriculture is mainly characterized by the types of fertilizers used (compost, vermicompost, animal manure, among others), which allow greater addition and retention of nutrients. In this sense, organic vineyards usually have higher levels of essential nutrients for the correct growth of the vine [13,14]. Likewise, by not using pesticides as a protective response to phytopathogens, the plant produces a greater production of secondary metabolites in the grapes, metabolites which have a high technological value in viticulture [11].

Currently, in Mexico, there are limited scientific studies investigating the influence of agricultural management in vineyards or the elemental profile of soils on the phenolic compound content in grapes [15–17]. In this context, the biosynthesis of bioactive compounds depends on the grape variety and the different factors that define the terroir of the region [18]. These compounds primarily develop in the skin and seeds of the grapes and have significant technological value in viticulture, as they influence the sensory properties, including the color and flavor of the produced wine [18,19]. Likewise, a higher content of bioactive compounds is closely linked to the functional properties of grapes, such as antioxidant capacity.

Based on the above, there is a lack of in-depth studies on the impact of agricultural management in vineyards and the elemental profile of their soils on the biosynthesis of bioactive compounds in grape skins and seeds. In this context, implementing organic agricultural management in viticulture could positively impact the quality of grapes used for winemaking. Therefore, this study aims to evaluate the relationship between agricultural management (organic and conventional) in vineyards, the elemental profile of their soils, and the quality of harvested Syrah and Tempranillo grapes, specifically focusing on the phenolic profile and antioxidant capacity in their skin and seed.

2. Materials and Methods

2.1. Chemicals and Reagents

The reagents and analytical-grade chemicals used in this study were obtained from Karal (Leon, Mexico), Sigma-Aldrich (Saint Louis, MO, USA), Thermo Fisher (Waltham, MA, USA), and Merck (Darmstadt, Germany).

2.2. Study Area

Two vineyards were selected in the state of Guanajuato, Mexico, with different agricultural management: conventional (CON) (21°12′29″ LN 100°51′08″ LO; Dolores Hidalgo Cuna de la Independencia Nacional) and organic (ORG) (20°54′33″ LN 100°40′45″ LO; San Miguel de Allende) (Figure 1). Regarding agrotechnical conditions, the CON vineyard used a drip irrigation system, chemical fertilization, and chemical fumigation. Meanwhile, the ORG vineyard has a drip irrigation system, fertilization from compost and animal manure, and netting to protect against birds and insects. In the case of the grape varieties studied, Syrah (SY) and Tempranillo (TE) grapes were selected for both vineyards. SY grapes are characterized by their bluish-black hue and medium size; they are also well adapted to different climates [18]. Meanwhile, TE grapes are characterized by their high sugar content and their bluish-black hue; in addition, they ripen early and develop better in places with high solar radiation [18]. On the other hand, the soils sampled from the CON belong to the physiographic province of the Sierra Madre Oriental, with average elevations of 2200 masl. The dominant rocks in the area are sandstones deposited over Pliocene rhyolitic tuffs, while Quaternary alluvial deposits dominate in the surrounding regions. In contrast, ORG soils are in the physiographic province of the Trans-Mexican Volcanic Belt [20], a geological environment characterized by volcanic domes with altitudes reaching 2000 masl. The dominant lithology consists of extrusive rocks, mainly Miocene basalts and Andesites, and extensive deposits of sandstones and conglomerates of Neogene (Pliocene) age. Figure 1 shows the soil map of the state of Guanajuato. Thus, the CON vineyard has Luvic Phaeozem and the ORG vineyard has Pellic Vertisol. The results obtained from the physicochemical properties of the different soils in this study coincide with the characteristics of both soil orders classified for the state [21].

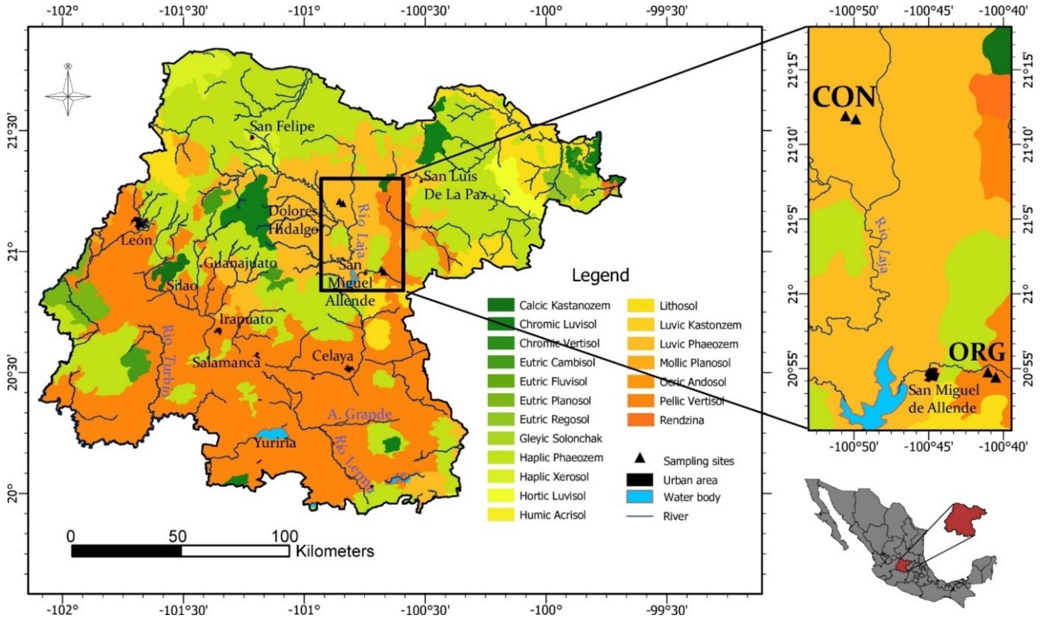

Figure 1. Soil map of the state of Guanajuato, indicating the soil samples obtained in the conventional (CON) and organic (ORG) vineyards.

The historical mean annual temperature, precipitation, and evaporation for the CON vineyard are 16.77 °C, 403.38 mm, and 1191.31 mm, respectively, with an annual water budget of −788.52 mm. For the ORG vineyard, the historical mean annual temperature, precipitation, and evaporation are 16.47 °C, 473.26 mm, and 1467.01 mm, respectively, resulting in an annual water balance of −993.75 mm. Additionally, during the vegetative period (March–August), the CON vineyard presented a mean temperature of 18.87 ± 1.30 °C, precipitation of 44.57 ± 30.53 mm, evaporation of 116.65 ± 12.97 mm, and a water balance of −72.08 ± 36.73 mm. Meanwhile, the ORG vineyard presented a mean temperature of 18.50 ± 1.19 °C, precipitation of 52.20 ± 36.27 mm, evaporation of 146.90 ± 14.82 mm, and a water balance of −94.70 ± 49.40 mm.

2.3. Grape and Soil Sampling

The soil and grape samplings were performed in July and August 2023 because, during these months, the grapes reach their optimal ripeness to be harvested. For soil, sampling and sample preparation were carried out following the NOM-021-SEMARNAT-2000 [22]. A zigzag sampling pattern was followed for each vineyard and plot studied, with three composite samples (each consisting of 20 subsamples) collected at a depth of 0–30 cm from the surface. On the other hand, SY and TE grapes were randomly harvested from the vines located on the surface where soil samples were taken. Grapes, from both vineyards, did not show the presence of *Botrytis cinerea*. Additionally, the vines from which the grapes were collected were planted in 2016 (7 years old).

2.4. Soil Analysis

2.4.1. Physicochemical Properties

The physicochemical properties of the soil were determined from the NOM-021-SEMARNAT-2000 [22]. Moisture content was determined by the gravimetric method at a temperature of 105 °C for 24 h. The soil color was obtained using the Munsell table. The particle size fractions (% clay, silt, and sand) were determined using the Bouyoucos method. Likewise, bulk density and true density were determined from the test tube and pycnometer method, respectively. The pH and electrical conductivity (EC) were measured at a 1:5 w/v ratio with distilled water using a potentiometer Orion Star A214 (Thermo Scientific™, Waltham, MA, USA) and a conductometer PC45 (Conductronic, Puebla, Mexico), respectively. The percentages of organic matter (OM) and calcium carbonate ($CaCO_3$) were obtained by the loss on ignition (LOI) method at 550 °C for 3 h and 950 °C for 2 h [23]. Moreover, the percentage of total nitrogen (N) was determined using the Kjeldahl method proposed in the NOM-021-SEMARNAT-2000 [22]. Finally, extractable phosphorus (P) was determined by spectrophotometry at a wavelength of 882 nm using the methodology proposed by Bray and Kurtz [24].

2.4.2. Elemental Profile Composition

The soil chemical composition was analyzed using an X NEX CG X-ray fluorescence spectrometer (Rigaku, Tokyo, Japan) with energy dispersion (EDXRF). This was conducted through an X-ray tube of Pd anode with a maximum power of 50 W, a voltage of 50 kV, and a current of 2 mA within a helium atmosphere. Calibration was performed using the standard MCA®. Soil samples were analyzed at a particle size of <75 microns.

2.5. Grape Analysis

2.5.1. Determination of Bioactive Compounds

Extraction of Bioactive Compounds

The methanolic extract used to determine total bioactive compounds was obtained through the manual separation of grape skins and seeds. Subsequently, the skins and seeds were crushed separately. A sampling of 5 g was added to 50 mL of methanol (80% v/v) and stirred for 1 h in the absence of light using a KS 3000 i control shaker (IKA, Wilmington, DE, USA). Finally, the mixture was placed in a C-40 centrifuge (SOL-BAT, Puebla, Mexico) for 15 min at 3500 rpm, and the supernatant was collected [25,26].

Total Phenolic Content

The determination of the total phenolic content (TPC) was carried out based on the methodology proposed by Gulcü et al. [27], with some modifications. An extract sample of 20 µL was combined with 480 µL of distilled water and 250 µL of 1 N Folin–Ciocalteu reagent, and the mixture was allowed to react for 8 min. Subsequently, 1250 µL of sodium carbonate (7.5%) was added and samples were left to rest for 1 h in the dark. Finally, the absorbance was measured at 765 nm using a Genesys 10S UV–vis spectrophotometer (Thermo Scientific™, Waltham, MA, USA). The results were expressed as milligrams of gallic acid equivalent per gram of dry sample (mg GAE/g DW).

Total Anthocyanin Content

The total anthocyanin content (TAC) was determined using the pH differential method, following the methodology proposed by Lee et al. [28], with some modifications. An extract aliquot of 500 µL was taken and 1750 µL of buffer pH 1 was added. Similarly, another 500 µL of the extract was taken, to which 1750 µL of pH 4.5 buffer was added. Both solutions were then allowed to stand for 15 min in the absence of light. Finally, absorbance readings were taken at 520 nm and 700 nm using a Genesys 10S UV–vis spectrophotometer (Thermo Scientific™, Waltham, MA, USA). The results were calculated and expressed in milligrams of cyanidin-3-glucoside per gram of dry sample (mg C3G/g DW) from Equation (1), as follows:

$$AC = \frac{(A)(MW)(DF)(VE)(1000)}{(\varepsilon)(1)(M)};\ A = (A_{510} - A_{700})_{pH1} - (A_{510} - A_{700})_{pH4.5} \quad (1)$$

where A is the differential of the absorbances measured at different pH, MW is the molecular weight of cyanidin-3-glucoside (449 g/mol), DF is the dilution factor, VE is the extract volume, ε is the molar extinction coefficient of cyanidin, and M is the mass of the food sample.

Condensed Tannins

The condensed tannins (CTs) content was determined following the methodology of Cheaib et al. [29], with some modifications. Aliquots of 1000 µL of the sample extract were added to two different tubes, followed by the addition of 500 µL of distilled water and 1500 µL of 12 N HCl. Then, one of the tubes was heated at 100 °C for 30 min, while the second tube was kept at room temperature. Subsequently, 250 µL of ethanol was added to each tube and the absorbance was measured at 520 nm using a Genesys 10S UV–vis spectrophotometer (Thermo Scientific™, Waltham, MA, USA). Results were calculated and expressed in milligrams per gram of dry sample (mg/g DW) from Equation (2), as follows:

$$Tannin\ concentration = (19.33)(Abs_1 - Abs_2) \quad (2)$$

where Abs_1 is the absorbance of the sample at room temperature and Abs_2 is the absorbance of the sample exposed to 100 °C.

Identification of Individual Phenolic Compounds

The identification of individual phenolic compounds in skins and seeds was performed using a Waters Separations Module e2695 high-performance liquid chromatography device (Conquer Scientific, Poway, CA, USA) equipped with a UV–vis detector 2489 (Waters, Milford, CT, USA) and a C18 column (2.7 µm, 3.0 × 100 mm) was used to identify and quantify the different polyphenols. Direct samples were filtered using a 25 mm sterile nylon filter with a pore size of 0.20 µm and were placed in 2 mL amber crimp vials for automated injection. Samples were analyzed at 280 nm, a flow rate of 0.30 mL/min, 20 °C, and 1500 psi, with a total run time of 45 min per sample. The phases used were acetonitrile (pure) and acidified water (0.2% acetic acid) in a gradient starting and ending at 0:100 (acetonitrile: acidified water), passing through 40:60. Methanol was used for washing. All phases were HPLC grade and prefiltered with a 47 mm nylon membrane filter with a pore size of 0.20 µm (Merck, Darmstadt, Germany). Data were processed using Empower 3 software (Waters, Milford, CT, USA). The Merck (Darmstadt, Germany) standards used were caffeic acid (CAS No. 331-39-5), catechin (CAS No. 225937-10-0), chlorogenic acid (CAS No. 327-97-9), ellagic acid (CAS No. 476-66-4), epicatechin (CAS No. 989-51-5), ferulic acid (CAS No. 537-98-4), gallic acid (CAS No. 149-91-7), kaempferol (CAS No. 520-18-3), myricetin (CAS No. 529-44-2), *p*-coumaric acid (CAS No. 501-98-4), quercetin (CAS No. 117-39-5), resveratrol (CAS No. 501-36-0), rutin (CAS No. 250249-75-3), syringic acid (CAS No. 530-57-4), and vanillic acid (CAS No. 121-34-6). Finally, the results were expressed in micrograms per milliliter of sample (µg/mL).

2.5.2. Determination of Antioxidant Capacity *In Vitro*

The antioxidant capacity in vitro was determined using the radical 2,2-diphenyl-1 pricrylhydrazyl (DPPH) inhibition methodology [30,31]. Starting from a 12×10^{-5} M dilution of the DPPH radical in methanol, the initial absorbance was measured at 515 nm. Afterward, 100 µL of the sample extract was added to 3900 µL of the DPPH solution. The solution was allowed to stand in the dark for 30 min, and then the absorbance reading was taken at 515 nm using a Genesys 10S UV–vis spectrophotometer (Thermo Scientific™, Waltham, MA, USA). Results were expressed in micromoles of Trolox equivalent per gram of dry sample (µmol Trolox eq/g DW).

2.6. Statistical Analysis

A multifactorial analysis of variance (ANOVA) was performed, considering agricultural management (CON and ORG) and grape variety (SY and TE) as the independent variables. Additionally, a *post-hoc* Tukey analysis was carried out using the Statgraphics Centurion XVI program (Statgraphics Technologies, Inc., Warrenton, VA, USA) to determine if there were significant differences ($p < 0.05$) between the wine regions. Subsequently, a principal component analysis (PCA) was performed using Jamovi 2.4.11 software (Jamovi, Sydney, Australia) to assess the correlations between the studied soil properties, the bioactive properties, and the antioxidant capacity in the skin and seed of the harvested grapes [16,32].

3. Results and Discussion

3.1. Physicochemical Properties and Chemical Composition in Soils

CON soils had ($p < 0.05$) 24.00% less moisture compared with ORG (Table 1). The values observed in both vineyards of this study are comparable with those reported for vineyard soils in Baja California, northern Mexico, where arid conditions prevail [16]. Similarly, the moisture obtained is consistent with the climate and the negative water deficit in the region under study (>−700 mm/year). On the other hand, the higher moisture content can be attributed to the greater amount of organic matter (OM) present in ORG soils (10.22 ± 1.10%). Thus, ORG soils exhibited 37.55% more OM ($p < 0.05$) compared with CON (6.38 ± 1.02%) (Table 1). Indeed, OM increases P and K levels while also enhancing the porosity and water retention capacity of vineyard soils [33]. Moreover, SY plots showed 16.63% more OM than TE. This would enhance the capacity to retain nutrients such as N, P, and other cations due to the formation of the clay–humic complex [34]. The N (0.27 ± 0.00%) and P (115.44 ± 9.50 mg/kg) contents in ORG plots were higher ($p < 0.05$) compared with CON (N: 0.23 ± 0.00% and P: 17.27 ± 13.08 mg/kg). Some authors have reported that N fertilization can reduce the exchangeable acidity (pH KCl) of the soil [35]. Regarding P, the percentages obtained are close to those indicated by Christou et al. [36] in conventional and organic vineyards [37]. In this sense, some organic fertilizers impact the availability of P, K, and N [38].

Table 1. Physicochemical properties in conventional (CON) and organic (ORG) vineyard soils for the Syrah (SY) and Tempranillo (TE) variety plots. The average ± standard deviation is shown.

	CON-SY	CON-TE	ORG-SY	ORG-TE
Moisture (%)	4.37 ± 0.14^{ay}	3.39 ± 0.16^{ax}	5.72 ± 0.22^{by}	4.50 ± 0.19^{bx}
Color	10YR 5/3 Brown	7.5YR 5/3 Brown	10YR 4/2 Dark grayish brown	7.5YR 3/2 Dark brown
Texture	Sandy clay loam	Sandy clay loam	Clay	Clay loam
Clay (%)	32.10 ± 1.64^{ay}	27.66 ± 2.45^{ax}	40.55 ± 3.53^{by}	31.70 ± 3.85^{bx}
Silt (%)	19.23 ± 1.33^{ax}	18.80 ± 3.13^{ax}	20.28 ± 3.38^{bx}	25.34 ± 3.37^{bx}
Sand (%)	48.67 ± 0.54^{bx}	53.55 ± 4.35^{by}	39.16 ± 0.53^{ax}	42.96 ± 2.12^{ay}
Bulk density (g/cm^3)	1.13 ± 0.02^{ax}	1.20 ± 0.02^{ay}	1.16 ± 0.02^{bx}	1.21 ± 0.03^{by}
Particle density (g/cm^3)	2.21 ± 0.03^{ax}	2.27 ± 0.02^{ax}	2.19 ± 0.02^{ax}	2.21 ± 0.05^{ax}
pH	8.27 ± 0.08^{bx}	8.34 ± 0.06^{bx}	7.77 ± 0.28^{ax}	7.99 ± 0.20^{ax}
EC (dS/m)	0.11 ± 0.01^{ax}	0.17 ± 0.02^{ax}	0.28 ± 0.06^{bx}	0.26 ± 0.05^{bx}
OM (%)	7.11 ± 0.27^{ay}	5.66 ± 0.17^{ax}	11.01 ± 0.24^{by}	9.44 ± 0.51^{bx}
$CaCO_3$ (%)	1.64 ± 0.05^{by}	1.62 ± 0.07^{bx}	1.13 ± 0.08^{ay}	0.97 ± 0.06^{ax}
N (%)	0.24 ± 0.01^{ax}	0.23 ± 0.01^{ax}	0.27 ± 0.01^{bx}	0.27 ± 0.01^{bx}
P (mg/kg)	26.52 ± 4.61^{ax}	8.01 ± 4.04^{ax}	122.16 ± 16.13^{bx}	108.72 ± 25.12^{bx}

Different superscripts between rows of the same column indicate a significant difference ($p < 0.05$) between treatments according to the Tukey test, where a and b are dependent on the vineyard management and x and y are dependent on the plot variety.

The CON vineyard plots presented a sandy clay loam texture (clay: 29.38 ± 2.43% and sand: 51.11 ± 3.45%). In the case of the ORG vineyard, the SY plot presented a clay texture (clay: 40.55 ± 3.53% and sand: 39.16 ± 0.53%) and the TE plot a clay loam texture (clay: 31.70 ± 3.85 and sand: 42.96 ± 2.12). Meanwhile, for the case of pH, CON soils had ($p < 0.05$) a more alkaline pH (8.31 ± 0.04) than ORG (7.88 ± 0.15). In this sense, the pH values are classified as medium alkaline according to the national standard. These results are similar to those reported in Mexican vineyards [16,39], where some authors mention that the ideal soil pH is between 5.5 and 8.0; therefore, all soils analyzed comply with this optimum pH. In the case of electrical conductivity (EC), soils from the ORG vineyard were found to be 48.17% more conductive ($p < 0.05$) when compared with CON. The EC presented by all the vineyards is low, which can be influenced by the content of fertilizers, humidity, and salinity of the area or by the natural washing of the soils and sediments of the catchment area [16,40].

Meanwhile, for $CaCO_3$ content, CON soils presented 35.34% more $CaCO_3$ ($p < 0.05$) compared with ORG. In this sense, calcium influences abscisic acid biosynthesis and stomata closure, which causes stress in the plant [41,42]. Likewise, the higher percentages of $CaCO_3$ in CON soils could be explained by the mineral's precipitation in the presence of Ca-rich parent material (rhyolites rich in amphiboles, pyroxenes, and plagioclases). This is accompanied by the high evaporation rates in the study area (CON: 1191.91 mm and ORG: 1467.01 mm).

Regarding the soil chemical composition, the influence of the parent material in the soils studied is reflected in the content of most oxides. Thus, CON plots had a higher content ($p < 0.05$) of MgO, CaO, SO_3, and K_2O, the latter due to the presence of acid igneous rocks with minerals rich in K (biotites). On the other hand, ORG plots presented higher contents ($p < 0.05$) of Fe_2O_3, MnO, TiO_2, and SiO_2 due to the presence of volcanic rocks rich in Fe, Mn, and Ti. Similarly to this research, Gaeta et al. [43] have reported high percentages of SiO_2, Al_2O_3, K_2O, CaO, and FeO in vineyard soils located in Monti Albano, Italy, where the dominant rocks in the area are pyroclastic rocks generated by volcanic eruptions. For both vineyards, the most abundant oxides were Al_2O_3 and SiO_2. Moreover, SY plots presented 10.08% more Al_2O_3 ($p < 0.05$) in comparison with TE (Table 2). Some authors mention that the excess of aluminum ions can reduce soil pH up to 5.5 [44]. Meanwhile, ORG soils presented 3.73% more SiO_2 ($p < 0.05$) than CON. In this sense, Si improves cell wall structure and increases resistance to drought, frost, and pests [45,46].

Table 2. Chemical composition in the soils of the conventional (CON) and organic (ORG) vineyards for the Syrah (SY) and Tempranillo (TE) variety plots. The average ± standard deviation is shown.

Oxides (%)	CON-SY	CON-TE	ORG-SY	ORG-TE
MgO	1.28 ± 0.28 ^{bx}	1.52 ± 0.26 ^{bx}	1.33 ± 0.02 ^{ax}	1.09 ± 0.03 ^{ax}
K_2O	2.75 ± 0.07 ^{bx}	3.63 ± 0.02 ^{by}	1.68 ± 0.04 ^{ax}	1.67 ± 0.04 ^{ay}
CaO	1.28 ± 0.10 ^{bx}	2.25 ± 0.09 ^{by}	1.61 ± 0.02 ^{ax}	1.58 ± 0.02 ^{ay}
Al_2O_3	18.63 ± 1.24 ^{ay}	17.87 ± 1.54 ^{ax}	19.70 ± 0.10 ^{ay}	16.60 ± 0.17 ^{ax}
SiO_2	68.80 ± 1.65 ^{ax}	67.77 ± 1.44 ^{ay}	68.93 ± 0.15 ^{bx}	72.93 ± 0.21 ^{by}
SO_3	0.74 ± 0.02 ^{bx}	0.76 ± 0.01 ^{bx}	0.74 ± 0.01 ^{ax}	0.74 ± 0.01 ^{ax}
TiO_2	0.65 ± 0.01 ^{ax}	0.63 ± 0.03 ^{ax}	1.17 ± 0.05 ^{bx}	1.20 ± 0.05 ^{bx}
MnO	0.08 ± 0.00 ^{ax}	0.05 ± 0.00 ^{ax}	0.10 ± 0.00 ^{bx}	0.13 ± 0.01 ^{bx}
Fe_2O_3	3.56 ± 0.08 ^{ay}	3.36 ± 0.17 ^{ax}	4.46 ± 0.04 ^{by}	3.76 ± 0.02 ^{bx}

Different superscripts between rows of the same column indicate a significant difference ($p < 0.05$) between treatments according to the Tukey test, where a and b are dependent on the vineyard management and x and y are dependent on the plot variety.

3.2. Bioactive Properties and Antioxidant Capacity in Grapes

Figure 2 shows the concentration of total bioactive compounds and antioxidant capacity in the skin and seed grapes. Regarding total phenolic content (TPC) (Figure 2A), ORG grapes (38.83 ± 1.82 mg GAE/g) presented 15.63% more TPC ($p < 0.05$) in their skin than CON (32.76 ± 1.00 mg GAE/g). This could be because plants grown in an organic system without pesticides produce more natural substances, such as TPCs, to protect themselves from pests [11,47]. In addition, SY grapes (36.79 ± 4.70 mg GAE/g) presented 5.43% more ($p < 0.05$) TPC in their skin compared with TE (34.79 ± 3.88 mg GAE/g); these results are in alignment with those reported by some authors in the skin of grapes of the Cabernet Sauvignon, Merlot, Feteasca Neagra, Pinot Noir, and Muscat Hamburg varieties [11,48,49].

On the other hand, CON grapes (34.26 ± 11.40 mg GAE/g) presented 20.01% more TPC ($p < 0.05$) in their seeds compared with ORG (27.40 ± 2.37 mg GAE/g) (Figure 2A). Additionally, TE grapes (35.7 ± 9.36 mg GAE/g) showed 27.28% more TPC in their seeds than SY (25.96 ± 0.33 mg GAE/g); these results are close to those indicated by Lorrain et al. [48,49] for Cabernet Sauvignon and Merlot grapes.

Regarding total anthocyanin content (TAC) in skin grapes (Figure 2B), no statistically significant difference was observed ($p > 0.05$). For the content of condensed tannins (CTs) (Figure 2C), ORG grapes (0.31 ± 0.13 mg/g) presented 49.33% more ($p < 0.05$) TC in their skin than CON (0.15 ± 0.01 mg/g). Likewise, SY grapes (0.28 ± 0.18 mg/g) showed 36.15% more ($p < 0.05$) TC in their skin compared with TE (0.18 ± 0.05 mg/g). In the case of the seed grapes, ORG grapes (1.31 ± 0.13 mg/g) presented 61.87% more ($p < 0.05$) TC in their seeds than CON (0.50 ± 0.09 mg/g), these results align with those reported by Bosso et al. [50] for grapes of the Nebbiolo variety (1.31 ± 0.13 mg/g).

Table 3 shows the content of individual phenolics detected through HPLC for skin and seed grapes. Thus, the skin of CON grapes presented higher percentages ($p < 0.05$) of caffeic acid (25.81%), catechin (22.96%), epicatechin (11.34%), ferulic acid (8.09%), syringic acid (28.81%), vanillic acid (7.74%), gallic acid (24.43%), and rutin (5.95%) in comparison with ORG. Our results coincide with those reported by Corrales et al. [51], who found a higher content of catechin and epicatechin in conventional grape skins compared with organic ones. Furthermore, other authors have mentioned that the higher content of Ca, Mg, and K_2O in soil positively impacts the biosynthesis of phenols (caffeic acid, ferulic acid, syringic acid, vanillic acid, and gallic acid) and flavonoids (rutin), this agrees with the higher contents of these elements in CON soils and grapes (Tables 2 and 3) [52]. Likewise, the skin of ORG grapes showed higher percentages of chlorogenic acid (5.26%), myricetin (21.60%), quercetin (30.59%), and resveratrol (19.17%) compared with CON. The results coincide with other reports that indicate a higher quercetin content in organic grape skins than in conventional ones [51,53]. Additionally, soil components (clay, pH, moisture, Al, Fe, among others) directly influence the content of flavonols in grapes, mainly quercetin, myricetin, and rutin [15]; reported values fall within their increased content in ORG soils and grapes (Tables 1–3). Regarding grape varieties, SY skin presented higher percentages ($p < 0.05$) of epicatechin (43.60%), myricetin (33.28%), rutin (25.55%), quercetin (67.95%), resveratrol (46.34%), ellagic acid (16.68%), and *p*-coumaric acid (16.19%) than TE. Therefore, the content of bioactive compounds depends directly on the grape variety, the rootstock (nutrient absorption), and the properties of the soil [53–55]. Thus, the SY variety has a higher content of phenolic compounds in drained soils with high Fe content [55], which coincides with our research (Table 2). Meanwhile, TE skin showed higher percentages ($p < 0.05$) of caffeic acid (9.97%), catechin (3.70%), chlorogenic acid (8.34%), and gallic acid (10.71%) compared with SY.

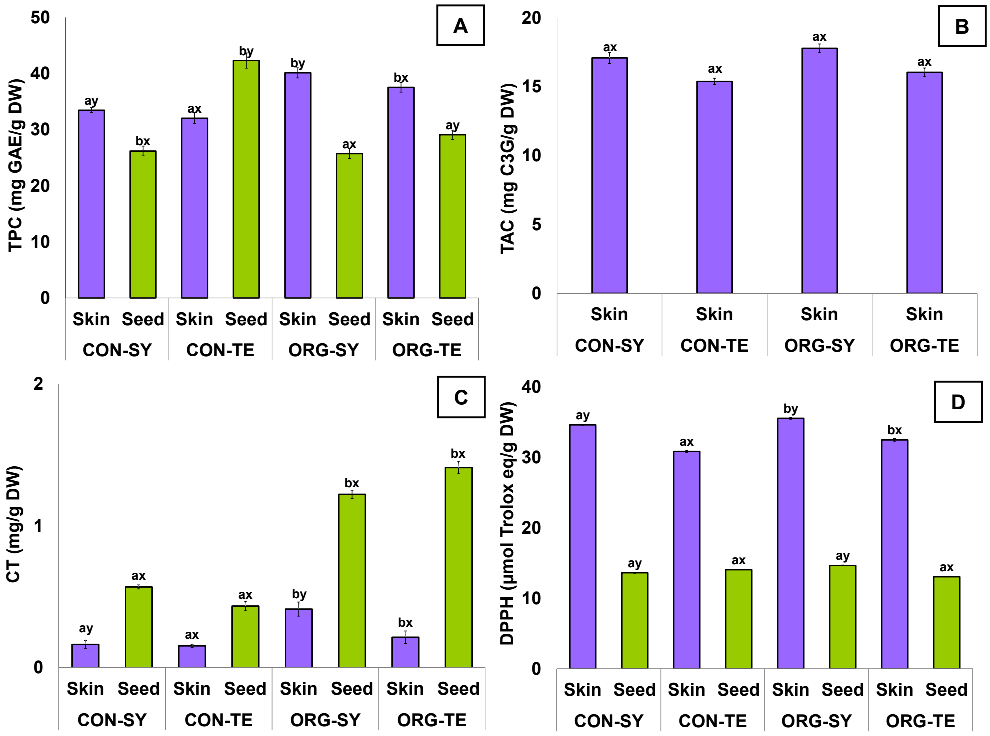

Figure 2. Total phenolic content (TPC) (**A**), total anthocyanin content (TAC) (**B**), condensed tannins (CTs) (**C**), and antioxidant capacity (DPPH) (**D**) in the skin and seed grapes from conventional (CON) and organic (ORG) vineyards for the Syrah (SY) and Tempranillo (TE) varieties. Different superscripts between rows of the same column indicate a significant difference ($p < 0.05$) between treatments according to the Tukey test, where a and b are dependent on the vineyard management and x and y are dependent on the variety.

Table 3. Content of individual phenols detected in the skin and seed of grapes from conventional (CON) and organic (ORG) vineyards for the Syrah (SY) and Tempranillo (TE) varieties. The average ± standard deviation is shown.

Compound (μg/mL)	**RT (min)**	**SKIN**				**SEED**			
		CON-SY	**CON-TE**	**ORG-SY**	**ORG-TE**	**CON-SY**	**CON-TE**	**ORG-SY**	**ORG-TE**
Phenolic acids									
Caffeic	11.70	24.92 ± 0.42 ^{bx}	38.09 ± 0.58 ^{by}	27.07 ± 0.86 ^{ax}	19.67 ± 2.89 ^{ay}	76.47 ± 1.94 ^{ay}	76.48 ± 0.94 ^{ax}	96.18 ± 4.49 ^{by}	74.36 ± 1.35 ^{bx}
Chlorogenic	11.15	230.06 ± 9.40 ^{ax}	314.81 ± 6.39 ^{ay}	305.56 ± 3.92 ^{bx}	269.61 ± 6.58 ^{by}	167.91 ± 5.79 ^{ay}	167.50 ± 7.64 ^{ax}	193.12 ± 2.20 ^{ay}	152.36 ± 2.83 ^{ax}
Ferulic	15.00	169.41 ± 2.73 ^{by}	94.28 ± 0.55 ^{bx}	161.85 ± 3.52 ^{ay}	80.48 ± 3.21 ^{ax}	344.70 ± 15.36 ^{ay}	309.78 ± 1.03 ^{ax}	375.54 ± 0.09 ^{by}	305.10 ± 1.85 ^{bx}
Gallic	1.62	60.40 ± 0.60 ^{bx}	88.42 ± 3.10 ^{by}	62.83 ± 0.57 ^{ax}	49.61 ± 3.51 ^{ay}	1389.86 ± 2.20 ^{ay}	1430.86 ± 8.49 ^{ax}	1769.34 ± 7.24 ^{by}	1485.48 ± 16.75 ^{bx}
P-coumaric	14.30	30.16 ± 1.72 ^{ay}	34.73 ± 2.86 ^{ax}	41.27 ± 1.96 ^{ay}	25.13 ± 1.57 ^{ax}	86.65 ± 2.88 ^{ay}	89.49 ± 3.37 ^{ax}	106.79 ± 5.68 ^{by}	93.63 ± 0.11 ^{bx}
Syringic	12.17	41.34 ± 0.91 ^{bx}	57.17 ± 3.27 ^{bx}	45.30 ± 1.90 ^{ax}	24.82 ± 0.85 ^{ax}	229.42 ± 3.39 ^{ay}	174.87 ± 3.27 ^{ax}	343.41 ± 8.05 ^{by}	150.15 ± 2.35 ^{bx}
Vanillic	11.62	42.98 ± 1.11 ^{bx}	60.76 ± 0.50 ^{bx}	55.36 ± 1.17 ^{ax}	40.35 ± 4.67 ^{ax}	72.76 ± 5.35 ^{ay}	70.93 ± 0.38 ^{ax}	83.77 ± 0.75 ^{by}	69.78 ± 3.66 ^{bx}
Flavonols									
Kaempferol	22.88	ND	ND	ND	ND	26.48 ± 2.61 ^{ax}	52.24 ± 1.38 ^{ay}	27.63 ± 63 ^{bx}	63.13 ± 0.01 ^{by}
Myricetin	17.21	136.06 ± 5.28 ^{ay}	106.23 ± 4.43 ^{ax}	194.65 ± 7.23 ^{by}	114.42 ± 8.97 ^{bx}	1024.75 ± 53.33 ^{ax}	1272.32 ± 0.16 ^{ay}	1336.62 ± 57.43 ^{bx}	1354.98 ± 9.12 ^{by}
Quercetin	19.90	25.19 ± 2.23 ^{ay}	11.81 ± 5.21 ^{ax}	51.06 ± 7.84 ^{by}	10.10 ± 2.49 ^{bx}	316.04 ± 34.93 ^{ax}	601.89 ± 16.37 ^{ay}	395.86 ± 3.18 ^{bx}	673.45 ± 3.39 ^{by}
Rutin	14.80	40.76 ± 1.02 ^{by}	33.75 ± 1.09 ^{bx}	42.13 ± 0.99 ^{ay}	27.95 ± 0.46 ^{ax}	198.05 ± 8.79 ^{ay}	170.61 ± 1.83 ^{ax}	225.32 ± 6.55 ^{by}	162.21 ± 5.63 ^{bx}
Flavanols									
Catechin	10.83	2091.67 ± 0.43 ^{bx}	2733.47 ± 8.63 ^{by}	2098.93 ± 11.34 ^{ax}	1618.29 ± 2.49 ^{ay}	438.88 ± 16.78 ^{by}	430.08 ± 1.89 ^{bx}	506.97 ± 12.41 ^{ay}	304.98 ± 2.53 ^{ax}
Epicatechin	12.50	203.56 ± 0.75 ^{by}	153.45 ± 2.58 ^{bx}	227.08 ± 5.90 ^{ay}	89.41 ± 2.68 ^{ax}	660.56 ± 0.36 ^{ay}	611.20 ± 2.79 ^{ax}	773.10 ± 3.99 ^{by}	578.26 ± 5.59 ^{bx}
Stilbene									
Resveratrol	18.57	28.95 ± 1.48 ^{ay}	22.62 ± 2.80 ^{ax}	46.14 ± 3.93 ^{by}	17.66 ± 1.42 ^{bx}	286.46 ± 25.11 ^{ax}	474.25 ± 6.25 ^{ay}	355.88 ± 1.73 ^{bx}	502.01 ± 3.18 ^{by}
Ellagitannin									
Ellagic acid	14.60	35.25 ± 0.49 ^{ay}	35.55 ± 3.57 ^{ax}	42.30 ± 2.10 ^{ay}	29.06 ± 2.13 ^{ax}	107.37 ± 3.21 ^{ay}	108.10 ± 2.44 ^{ax}	131.50 ± 5.30 ^{by}	112.52 ± 1.24 ^{bx}

Different superscripts between rows of the same column indicate a significant difference ($p < 0.05$) between treatments according to the Tukey test, where a and b are dependent on the vineyard management and x and y are dependent on the variety. RT: Retention time, ND: Not detectable.

ORG seeds presented higher percentages ($p < 0.05$) of caffeic acid (10.31%), ellagic acid (11.69%), epicatechin (5.82%), ferulic acid (3.84%), gallic acid (13. 33%), kaempferol (13.25%), rutin (4.87%), myricetin (14.65%), *p*-coumaric acid (12.11%), quercetin (14.15%), resveratrol (11.32%), syringic acid (18.08%), and vanillic acid (6.42%) compared with CON (Table 3). The vine synthesizes quercetin, kaempferol, and ellagic acid to protect against pathogens. Therefore, organic management that does not use pesticides tends to produce more compounds [56]. Regarding the grape variety, SY seeds presented higher percentages ($p < 0.05$) of caffeic acid (12.63%), catechin (22.28%), ellagic acid (7.64%), epicatechin (17. 03%), ferulic acid (14.62%), gallic acid (7.68%), rutin (21.38%), *p*-coumaric acid (5.33%), syringic acid (43.26%), and vanillic acid (10.10%) than TE. There is a competitiveness between the synthesis of flavonoids in seed and skin; in this sense, the heavier the seed of the fruit, the lower the flavanols content in the skin [57]. This behavior can be seen directly in the higher content of epicatechin in seed and catechin in skin. Finally, TE seeds showed higher percentages ($p < 0.05$) of kaempferol (53.09%), myricetin (10.12%), quercetin (44.17%), and resveratrol (34.20%) compared with SY. The higher content of individual compounds in TE skin and seed can be directly related to the lower percentages of moisture and OM in the soil (Table 1). Thus, the better OM and moisture contents in the soil cause water stress in the plant, which influences the greater biosynthesis of phenolic compounds [58].

In the case of antioxidant capacity (Figure 2D), no significant ($p > 0.05$) differences were found between the seeds of the grapes from the different agricultural managements. Meanwhile, ORG skin (34.04 ± 2.17 µmol Trolox equivalent/g) presented 3.77% more ($p < 0.05$) antioxidant capacity than CON (32.75 ± 2.65 µmol Trolox equivalent/g). Moreover, SY grapes (35.10 ± 0.67 µmol Trolox equivalent/g) presented 9.71% more antioxidant capacity in their skin than TE (31.69 ± 1.15 µmol Trolox equivalent/g). Moreover, SY seeds (14.15 ± 0.73 µmol Trolox equivalent/g) presented 4.09% more ($p < 0.05$) antioxidant capacity than TE (13.57 ± 0.71 µmol Trolox equivalent/g). Therefore, bioactive compounds capture free radicals, preventing oxidation processes [59]. Therefore, the greater antioxidant capacity in the SY variety can be directly explained by its greater content of individual phenols (Table 3).

3.3. Principal Component Analysis

Figure 3 shows the PCA for the correlation between soil properties, individual phenolic profile, and antioxidant capacity in skin grapes. The first two principal components explained 74.20% of the total variance (42.70% and 31.50%, respectively).

The first component presented a strong positive correlation (>0.60) with pH, sand, $CaCO_3$, MgO, K_2O, CaO, SO_3 in soil, and the content of catechin, gallic acid, vanillic acid, caffeic acid, and syringic acid in the skin grape. Likewise, a negative correlation (>-0.60) of these compounds with moisture, OM, EC, silt, P, SiO_2, TiO_2, MnO, and Fe_2O_3 in soil was found. Soil pH is crucial because plant nutrient availability depends on it [60]. Acuña-Avila et al. [16] reported a strong correlation between soil pH and Ca content. Likewise, the correlation between SiO_2 and Fe_2O_3 suggests the presence of clay minerals, which allow for the higher retention of nutrients in the soil [61]. Meanwhile, the second component presented a strong (>0.60) positive correlation with moisture, clay, OM, Al_2O_3, and Fe_2O_3 in soil, and the content of epicatechin, quercetin, resveratrol, rutin, *p*-coumaric acid, ellagic acid, ferulic acid, myricetin, and antioxidant capacity in the skin grape. These results coincide with those reported by Perin et al. [15], who found a strong positive correlation between the percentage of clay, moisture, Al, and Fe in soil with the content of quercetin, rutin, and myricetin in grape skin. Some authors have mentioned that a moderate concentration of Fe in the soil allows a higher biosynthesis of some bioactive compounds such as anthocyanins, flavonoids (quercetin and rutin), and flavonoids (epicatechin and myricetin), which have a strong antioxidant power [59,62,63]. Therefore, the antioxidant capacity of phenols depends directly on their structure, the number of hydroxyl groups, and the nature of their aromatic ring [59,64]. This could explain the clustering and positive correlation between these variables.

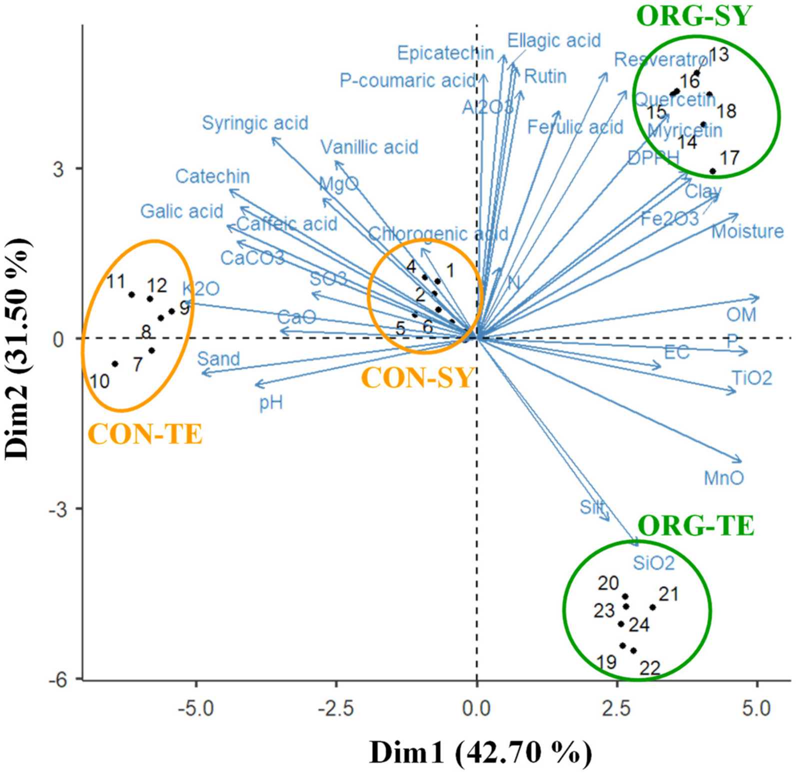

Figure 3. Principal component analysis (PCA) for soil characteristics and bioactive properties and antioxidants of grape skin. Circles indicate the treatments for the conventional (CON) and organic (ORG) vineyard for the Syrah (SY) and Tempranillo (TE) varieties.

Regarding the distribution of the experimental points (Figure 3), the organic vineyard treatments (ORG-SY and ORG-TE) suggest higher contents of moisture, clay, OM, N, Fe_2O_3, SiO_2, MnO, TiO_2 in soil and quercetin, myricetin, resveratrol, and antioxidant capacity in the skin. Moisture is related to vine water stress, which affects N metabolism and assimilation, influencing the quality of the grapes and wine that are produced [58,65]. Soil moisture is crucial in viticulture, as water scarcity severely limits grape production for winemaking [65]. In the case of the conventional vineyard (CON-SY and CON-TE), the distribution of the experimental points suggests higher contents of sand, $CaCO_3$, MgO, K_2O, CaO, and SO_3; a more alkaline pH in soil; and catechin, vanillic acid, syringic acid, caffeic acid, and gallic acid in the skin grape. Picone et al. [66] have reported lower caffeic acid content in grapes from vineyards with organic and biodynamic agricultural management. In addition, Yan et al. [67] have indicated that elemental composition and soil texture directly influence the quality of grapes used in winemaking.

Figure 4 shows the PCA for the correlation between soil properties, individual phenolic profile, and antioxidant capacity in seed grapes. The first two principal components explained 76.60% of the variance (47.50% and 29.10%, respectively). In this sense, the first component presented a strong positive correlation (>0.60) with moisture, clay, Al_2O_3, and Fe_2O_3 in soil, and the content of catechin, myricetin, rutin, gallic acid, chlorogenic acid, vanillic acid, caffeic acid, syringic acid, epicatechin, ellagic acid, ferulic acid, and antioxidant capacity in seed grapes. Likewise, a negative correlation (>-0.60) of these compounds with silt and SiO_2 in soil and resveratrol, quercetin, and kaempferol in seed was found. Thus, ferric and ferrous ions interact as cofactors in the activity of cytochrome P450 enzymes. These are responsible for several reactions in the pathways of some secondary metabolites (shikimic, malonic, mevalonic acid, and methylerythritol phosphate pathways) [68,69]. On the other hand, a study conducted in Mexican vineyards has reported a strong correlation between antioxidant capacity and the catechin, epicatechin, and gallic acid content in grapes [16]. These same authors mention a negative correlation between Al and Fe in soil with quercetin and resveratrol biosynthesis, which coincides with the results of our study [15]. Meanwhile, the second component presented a strong (>0.60) positive correlation with moisture, EC, clay, silt, OM, P, SiO_2, TiO_2, MnO, and Fe_2O_3 in soil, and the content of myricetin, gallic acid, *p*-coumaric acid and ellagic acid in seed grapes. Moreover, a negative correlation (>−0.60) between these compounds and pH, sand, MgO, K_2O, and $CaCO_3$ in the soil was found. Thus, some studies have reported that some elements, such as Sr, Pb, Si, and Mn, induce stress in the vine, influencing the biosynthesis of several phenols [70,71]. In addition, soil sand and Mg content can negatively impact grapes' myricetin content. However, phosphorus is related to the biosynthesis of flavonols such as myricetin. Likewise, several studies have indicated that some heavy metals, such as Mn, induce stress in the plant, causing an increase in the enzymatic activity involved in the biosynthesis of bioactive compounds [16,70].

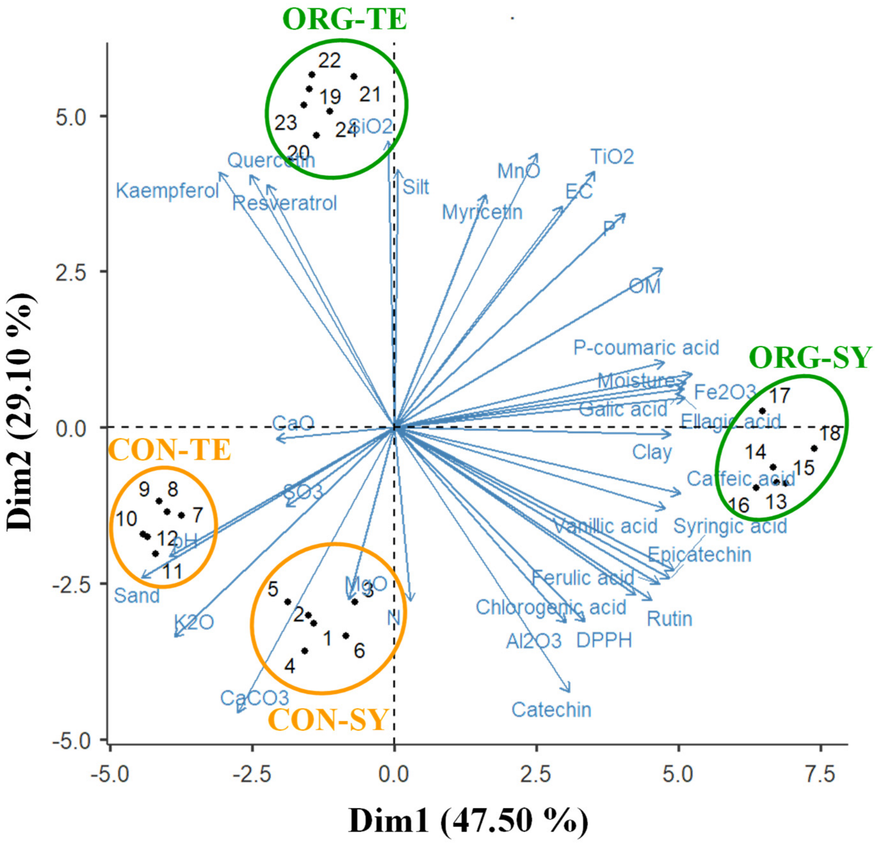

Figure 4. Principal component analysis (PCA) for soil characteristics and bioactive properties and antioxidants of grape seeds. Circles indicate the treatments for the conventional (CON) and organic (ORG) vineyard for the Syrah (SY) and Tempranillo (TE) varieties.

Regarding the distribution of the experimental points (Figure 4), most of the response variables were directed towards the organic vineyard groups (ORG-SY and ORG-TE). Thus, the organic vineyard treatments (ORG-SY and ORG-TE) suggest higher contents of moisture, clay, silt, EC, OM, SiO_2, Fe_2O_3, MnO in soil and epicatechin, rutin, resveratrol, kaempferol, quercetin, myricetin, gallic acid, ellagic acid, caffeic acid, vanillic acid, syringic acid, ferulic acid, *p*-coumaric acid, and CT in seed. Kaur et al. [72] have reported an increase in the amount of P when minerals and organic fertilizers were combined, which could explain the higher percentage of P in the ORG vineyard. Likewise, organic management increases microbial activity and mass, increasing soil P content [73]. On the other hand, several studies have reported higher concentrations of phenolic compounds in grapes, apples, blueberries, and raspberries harvested in organic systems, which coincides with that reported in the present study [17,74–76]. In the case of the conventional vineyard (CON-SY and CON-TE), the distribution of the experimental points suggests higher percentages of sand, MgO, $CaCO_3$, K_2O, SO_3, and CaO, and more alkaline soil pH. Oliver et al. [60] have mentioned that soils with higher acidity present deficiencies of nutrients such as Ca, K, P, and Mg; in this sense, the CON vineyard soils are those that presented lower acidity.

4. Conclusions

The present study has shown that organic agricultural management and soil properties positively influence the biosynthesis of bioactive compounds in grape skin and seed. Thus, the clay–humic complex allowed the ORG vineyard to have higher moisture, clay, silt, EC, OM, P, N, Fe_2O_3, SiO_2, MnO, and TiO_2 contents in the soil. This allowed the grapes harvested in ORG to exhibit a superior development of myricetin, quercetin, resveratrol, chlorogenic acid, and antioxidant capacity in the skin. However, except for catechin and chlorogenic acid, ORG seeds showed higher concentrations of most phenolic compounds. On the other hand, SY grapes showed higher individual phenolic content. Meanwhile, soil pH, clay, sand, OM, $CaCO_3$, and oxides (Al_2O_3, K_2O, SO_3, MgO, and CaO) positively influenced the biosynthesis of individual phenolics and the skin's antioxidant capacity. Meanwhile, moisture, clay, EC, OM, P, and oxides (SiO_2, TiO_2, Al_2O_3, Fe_2O_3, and MnO) in soil positively influenced the individual phenolic content in seeds, except for resveratrol, quercetin, and kaempferol. These results demonstrate the potential of organically managed farming for producing high-quality grapes for winemaking. Finally, future research should investigate the impact of agricultural management on the physicochemical, microbiological, and sensory properties of grapes for winemaking.

Author Contributions: F.M.-G.: Writing—original draft, validation, methodology, investigation, formal analysis, data curation. T.A.Q.-M.: Methodology, data curation, supervision, writing—review and editing. R.M.-A.: Methodology, supervision, writing—review and editing. L.F.R.-S.: Methodology, data curation, supervision, writing—review and editing. G.A.Z.: Conceptualization, funding acquisition, methodology, project administration, resources, supervision, writing—review and editing. C.O.: Conceptualization, funding acquisition, methodology, project administration, resources, supervision, writing—review and editing. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Data Availability Statement: The data presented in this study are available upon request from the corresponding author.

Acknowledgments: F. Macías-Gallardo (Grant Number: 1201868) thanks the Secretaría de Ciencia, Humanidades, Tecnología e Innovación (Mexico) for their support of his Master's studies in Biosciences at the Universidad de Guanajuato. The authors thank the Secretaría de Turismo del Estado de Guanajuato (Mexico).

Conflicts of Interest: The authors declare no conflicts of interest.

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