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Evaluation of the Profiles of Essential and Potentially Toxic Elements Present in Grape Must Grown and Soil from the Region Submedium São Francisco, Brazil

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This work evaluated the multi-element concentration in grape must and soil samples employing inductively coupled plasma optical emission spectrometry (ICP OES), after microwave-assisted digestion. The study aimed to establish a profile of seven grape varieties produced in Petrolina, region Submedium São Francisco, Brazil. Principal component analysis (PCA) clearly showed a good separation of samples in terms of mineral constituents. Although some soil samples showed concentrations of Co, Cu and Ni higher than the prevention values (VP), no sample exceeded the values stipulated for an intervention in agricultural soils based on Resolution No. 420/2009 of the National Council for the Environment (CONAMA). So, the results obtained contribute to food mineral composition table, as it brings unprecedented information about the concentration of the elements in seven grape varieties, providing indicators of geographic location, and contributing to the preliminary construction of a geochemical base of the regional soil.

Keywords: grape must, soil, mineral composition, geochemical base, principal component analysis

Introduction

Brazilian viticulture is characterized mainly by variation in cultivars and in production systems, due to the great environmental diversity among the production zones, soil variability, land structure, and mainly, the climates of the growing regions, ranging from temperate to subtropical and tropical.[1] One of the main centers of tropical viticulture in Brazil is the Submedium São Francisco valley region. In this region, the semi-arid tropical climate, with favorable edaphoclimatic conditions, intense photoperiod and irrigation system developed with high technology, increased the physiological processes of the vines, making it possible, depending on the variety, to harvest about 2.5 harvests annually.[2,3]

Grapes *in natura* are among the most consumed fruits in the world, having an annual production growth rate close to 13% in the last decades.[4] It is rich in carbohydrates, vitamins and chemical elements, such as Ca, Cu, Fe, K, Mg and P, which are essential for human life.[5] In addition, potentially toxic elements can also be found and can present a toxic degree for organisms from a maximum concentration stipulated by health institutions.[6]

The quantification of essential and potentially toxic elements in grapes is timely, it can serve to increase the production and quality of the grapes produced for the consumer market. In addition, it can make it possible to establish a profile of the different types of grapes produced in the region, even indicating the region of production, as well as contributing to food composition tables.

The presence of essential and potentially toxic elements in grapes depends on several factors and environmental conditions.[3] The chemical elements resulting from

anthropic activities, such as unbridled agricultural expansion, contaminated irrigation water, industrial discharges, unrestricted use of fertilizers, pesticides and herbicides, can collaborate to increase the concentration of certain elements in the soil beyond the baseline levels (background).[7] In addition, the elements being able to be mobilized, leached or accumulated, and turn the soil into a possible source of contamination for grapes.[3] The concentrations of chemical elements in the soil also depends on the characteristics of the formation rock, pH, organic matter content, type of vegetation, geology, climate, physiological processes of microorganisms, vegetation, hydrological processes, among others.[8,9]

For this reason, several studies[8,10] have been developed to establish values of regional geochemical basis (RGB) through the values of baseline levels, that can be estimated either by obtaining baseline values of the soil components of the area under study or by using geochemical normalization technique, in order to differentiate anthropic and natural sources of the elements. The determination of RGB values contributes to support the monitoring of possible contaminants in the environment, and consequently, it makes it possible to promote management measures to reduce possible damage to the environment and human health.[11]

Among the various techniques used to determine geochemical normalization, there is the exploration of the linear regression analysis, which uses mathematical correlations between the concentration of the chemical elements and concentration of normalizing or reference element, which generally has lithogenic origin in the soil, such as Al, Fe, Li or Mn. The normalizing element has the characteristics of either undergoing minimal variations or being present in the soil in high concentrations.[8]

Thus, among the various ways of investigating the possible levels of contamination in the soil of vine cultivation and relating the background values with the concentration of the chemical element in the sample, there are the calculations of enrichment factors (EF) and geoaccumulation indexes (I_{geo}).[8,9,12]

The quantification of essential and potentially toxic elements in food and soil by spectroanalytical techniques is widely used in the literature.[13-17] Grape and the soil have high content of organic matter and, for insertion of this type of sample, it is generally required to apply a sample preparation procedure, since the matrix composition can cause spectral and non-spectral interferences.[18]

The use of acid decomposition systems for the sample preparation using microwave energy as a heating source is a more efficient, faster and safer process that uses small volumes of reagents compared to conductive heating.[19] In the literature, the experimental conditions of microwave-assisted decomposition of grape samples, such as quantities, combinations of reagents or program (temperature, time and power) on the optimization and validation process are described in a varied and/or succinct way.[20-23]

In addition, principal component analysis (PCA) had been frequently used in food and environmental chemistry to evaluate a large amount of data, with the indication of the main trends in the variability of observations.[24,25]

In this context, the objective of this study was to investigate the distribution of essential and potentially toxic elements in samples of grape must and grape growing soil, using inductively coupled plasma optical emission spectrometry (ICP OES), to establish a profile of the different types of grapes produced in the region Submedium São Francisco, Northeast, Brazil, through the application of the PCA. As well, as analyzing the ability of the glassware to transport elements from the soil to the grape. In addition, the background values of the studied chemical elements were estimated through linear regression analysis and geochemical normalization, where the soil contamination levels of the grape growing area were evaluated through the classifications established with the enrichment factor and geoaccumulation index.

Experimental

Sampling of grapes and soil

Grape and soil samples were collected from three farms located in the region Submedium São Francisco, Northeast, Brazil. At farm 1, samples were collected from the grape varieties Italy Moscato and "*Itália Melhorada*"; on farm 2 the Arra-15 and Scarlotta varieties, and on farm 3 the Crimson, Benitaka and BRS Isis varieties. The respective geographic coordinates of the farms are farm 1 (latitude 9° 18'47" S, longitude 40°33'54"W); farm 2 (latitude 9°18'05"S, longitude 40°26'36"W) and farm 3 (latitude 9°19'13"S, longitude 40°35'11"W). Sampling model was proposed and, in each cultivation area, five distinct points were selected aiming at a better strategy for studying the dynamics of the process of retention and mobilization of chemical elements in the soil and in the grape. Considering that the cultivation areas of each grape variety had different sizes of hectares, the distance between the sampling points varied in relation to the size of each area. Samples of grapes of seven varieties were collected in five points in each cultivation area, totaling 35 samples of grapes. The same collection points for grape samples were also assigned for the collection of soil samples, which also totaled 35 samples.

At each point, three bunches of grape samples were randomly collected outside and in the center of the plant during the harvest period. Then, from each cluster, around fifteen berries were removed from the top, middle and bottom of the cluster.[26] Subsequently, the grape musts were prepared by manually crushing the berries in decontaminated plastic bags, the seeds and skins were separated by decanting, the juice were transferred to polyethylene pots and sent for analytical procedures.[18]

The soil samples were collected in the grape growing area based on the collection procedure of the Brazilian Agricultural Research Corporation (Empresa Brasileira de Pesquisa Apropecuária, EMBRAPA).[27] In the laboratory, soil samples were dried in an oven at 60 ºC for 24 h. The samples were milled in a tungsten carbide ball mill (model Spex-Sampleprep, 8000M, Mixer/Mill, Metuchen, New Jersey, USA) for about 2 min (particles size 63 µm). Once ground, the soil samples were stored in previously decontaminated plastic containers.

Instrumentation

An inductively coupled plasma optical emission spectrometer with axial configuration (Vista Pro Varian, Mulgrave, Australia) equipped with solid state detector with charge coupled device (CCD) was used. The experimental conditions were established as the manufacturer recommendations, shown in Table 1. For sample introduction, a seaspray concentric nebulizer coupled cyclonic type nebulizer chamber was employed.

Table 1. Instrumental parameters for ICP OES determinations

Characteristics and parameters	Specification
Radiofrequency power / W	1200
Gas flow-rate of plasma / (L min^{-1})	15
Gas flow-rate of auxiliary / (L min^{-1})	1.5
Gas flow-rate of nebulizer / (L min^{-1})	0.70
Analytical wavelength / nm	Al (396.152), As (188.980), C (193.025), Ca (317.933), Cu (324.754), Fe (234.350), K (766.491), Mg (279.553), Mn (257.610), Se (196.026), Zn (213.857) in grape must samples; and C (193.025), Co (228.615), Cu (324.754), Fe (234.350), Ni (216.555), Pb (220.353), V (311.837), Zn (213.857) in soil samples

A microwave oven with cavity (model Start D, Milestone, Bergamo, Italy) composed of 12 closed tubes of the perfluoroalcoxi polymer (PFA) with volume of 100 mL and suitable for high pressure heating was used for decomposition of grape must and soil samples.

Reagents and solutions

All reagents were of analytical grade. The following reagents were used in the experimental procedures: nitric acid 65% m m^{-1} (HNO$_3$, Merck, Darmstadt, Germany), hydrochloric acid 37% m m^{-1} (HCl, Merck, Darmstadt, Germany), 30% hydrogen peroxide m m^{-1} (H$_2$O$_2$, Merck, Darmstadt, Germany), potassium chloride (KCl, Merck, Darmstadt, Germany) and citric acid (C$_6$H$_8$O$_7$, Merck, Darmstadt, Germany).

The multi-elementary solutions used were prepared from a stock solution containing 1000 mg L^{-1} (Specsol, Quimilab, São Paulo, Brazil) for Al, As, Co, Cu, Fe, Mn, Ni, Pb, Se, V and Zn and 4000 mg L^{-1} for Ca, K and Mg (Specsol). To determine dissolved organic carbon, a reference solution of 5000 mg L^{-1} of carbon was prepared from citric acid.

All solutions were prepared with deionized water, with a specific resistivity of 18.2 MΩ cm, obtained by Milli-Q® purification system (Millipore, Bedford, MA, USA). For the evaluation of the accuracy of the analytical method, it was analyzed the certified reference material of soil (San Joaquin Soil, NIST 2709a), acquired by National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA).

Procedure for analysis of grape must samples

The procedure for decomposing grape must samples followed the procedure proposed by Catarino *et al.*[18] A volume of 2.0 mL of the grape must sample, plus addition of 1.0 mL of HNO$_3$ (65% m m^{-1}), 4.0 mL of H$_2$O and 1.0 mL of H$_2$O$_2$ (30% m m^{-1}) were mixed for PFA flask. The microwave oven heating program was performed in four successive steps. In the first step, the temperature was increased to 100 °C over 8.5 min. In the second step, the temperature was held at 100 °C for 5 min. In the third step, the temperature was increased linearly to 180 °C over 8.5 min, then in the last step, the temperature was held at 180 °C for 10 min. Finally, ventilation was performed for 15 min before removing the microwave digestion rotor from the microwave oven. After the digestion procedure and subsequent cooling, the digested samples and blank solutions were diluted to a final volume of 15.0 mL with deionized water. Blanks solutions were prepared for each lot of samples, with all experiments performed in triplicate. Sample analyses were performed by ICP OES.

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Pseudo decomposition-total soil samples

The procedure for extraction of the inorganic constituents in soil samples followed the Method EPA 3051a of the U.S. Environmental Protection Agency (USEPA),[28] recommended by Resolution No. 420/2009 of the National Council for the Environment (Conselho Nacional de Meio Ambiente-CONAMA).[29]

According to the procedure, about 0.25 g of dry soil was initially measured in PFA flask. Then, a volume of 12 mL of inverted aqua regia (9 mL HNO_3 65% m m^{-1} plus 3 mL HCl 37% m m^{-1}) were added. The samples went through pre-extraction during 10 to 20 min. The microwave oven heating program for the decomposition of the soil samples was also carried out in four successive steps. In the first step, the temperature was increased to 100 °C over 3 min. In the second step, the temperature was held at 100 °C for 2 min. In the third step, the temperature was increased linearly to 180 °C over 5 min, then in the last step, the temperature was held at 180 °C for 10 min. Finally, ventilation was performed for 15 min before removing the microwave digestion rotor from the microwave oven.

After the process, the samples were transferred to 50 mL polypropylene plastic volumetric tubes, and volume completed to 40 mL with deionized water. Then, the tubes containing the samples were centrifuged at 2500 rpm during 10 min, the supernatant was transferred quantitatively, soon after, the elements were determined by ICP OES.

Procedure for determining the pH of soil samples in potassium chloride solution

The pH determinations of soil in potassium chloride solution were based on the manual of methods analysis established by EMBRAPA.[27] The mixture was subjected to agitation in the ultrasonic bath (model E15H, Elmasonic, brand Elma, Singen, Germany) during 30 min and value of pH of the supernatant was determined using pHmeter (Model Starter 3100, brand Ohaus). The pH measurements were performed in triplicates.

Evaluation of the geochemical base, enrichment factor and the geoaccumulation index

There is a lack of information on the background levels of the vine growing area in the Petrolina region, Northeast, Pernambuco, Brazil. In this work, theoretical background values were calculated for Cu, Co, Mn, Zn, Ni, Pb and V present in surface soils, through graphs for linear regression analysis with a 95% confidence interval, in order to build a geochemical base (RGB) specific to the study area.

The results obtained for approximately 21 soil samples (3 points *per* area) were selected to construct the graphs of each chemical element according to the normalizing element selected using the Statistica version 6.0 program (StatSoft, Tulsa, USA).[30] The chemical element enrichment factor was calculated using equation 1. The results obtained were compared with the levels of contamination intensity proposed by Hakanson.[31]

$$EF = \frac{\left(\dfrac{C_M}{C_{EF}}\right)_{Sample}}{\left(\dfrac{C_M}{C_{EF}}\right)_{Background}} \tag{1}$$

where, EF is the enrichment factor; $\left(\dfrac{C_M}{C_{EF}}\right)_{Sample}$ the ratio of the element and EF concentrations in the sample and $\left(\dfrac{C_M}{C_{EF}}\right)_{Background}$ the ratio between the element and EF background concentrations.

The geoaccumulation index (I_{geo}), was calculated using equation 2 and was described by Müller.[32]

$$I_{geo} = \log_2\left[\frac{C_n}{1.5C_{Bn}}\right] \tag{2}$$

where, C_n is the concentration of the chemical element measured; C_{Bn} is the concentration of the geochemical background, considering the concentration of the chemical element in the linear regression line and the factor 1.5 corresponding to the constant of lithogenic variability.

Multivariate data analysis

The interpretation of the experimental results generated from the different analysis of the grape must and soil samples was performed. The multivariate data analysis using principal component analysis (PCA) using Statistical Package for the Social Sciences program (SPSS, Chicago, IL, USA) was employed in the data analysis.[33]

For PCA application, data matrices with rows and columns of varying sizes were generated by varimax rotation method with Kaiser normalization.[34] The lines correspond to the sampling points of grape must or soil (cases) and the columns correspond to the variables studied for each case.

Results and Discussion

Analytical method

Analytical methods used to determine essential and

potentially toxic elements in grape must and soil samples were validated through the following figures of merit: limit of detection (LOD), limit of quantification (LOQ), linear dynamic range, accuracy and precision. The LOD and LOQ values were obtained from standard deviation of the intensities of ten analytical blank solutions, being between 0.01 (Mn) and 0.9 (Ca) mg L^{-1} for LOD, and between 0.03 (Mn) and 2.7 (Ca) mg L^{-1} for LOQ.

The precision of the analytical method was expressed from the relative standard deviation (RSD) for 10 samples of the proposed procedure of digestion of a grape must sample, being obtained RSD values less than 7% (n = 3). The accuracy of the method was performed through addition and recovery tests, with three levels of concentration of analyte addition (0.5, 1.0 and 2.0 mg L^{-1}), in triplicate. The percentages of recoveries obtained for the chemical elements in the grape must samples varied between 81.0 ± 0.1 and 119.0 ± 0.8%, being considered within the acceptable range recommended for quantitative chemical analysis.[18,21] The proposed microwave-assisted digestion sample using diluted HNO$_3$ and showed low reagent consumption (1.0 mL HNO$_3$ and 1.0 mL H$_2$O$_2$), and low levels of dissolved organic carbon (< 2% m v^{-1}) and low residual acid concentration (0.93 mol L^{-1}).

The LOD and LOQ values obtained for the pseudo-decomposition procedure of the soil varied from 0.1 for Mn to 1.3 for Fe, and 0.4 for Mn µg g^{-1} to 3.8 for Fe µg g^{-1}, respectively, for analytical method. For the analysis of 10 replicates of a soil sample, RSD values below than 9% (n = 10) was obtained. The accuracy of the proposed method was confirmed through the analysis of certified reference material (CRM) of San Joaquin soil (NIST 2709a). The values obtained using the CRM, mean and 95% confidence interval for triplicate, were compared to certified values, with variation between 79 ± 7 and 112 ± 2% (n = 3), being accepted for quantitative analysis. These values are considered satisfactory and are in accordance to Association of Official Analytical Chemists.

Determination and evaluation of essential and potentially toxic elements in grape must

Table 2 presents the concentrations of the essential elements (Ca, Cu, Fe, K, Mg, Mn, Se and Zn) and potentially toxic (As, Al and Se) in the 7 varieties of grape must samples (Italy Moscato, "*Itália Melhorada*", Arra-15, Scarlotta, Crimson, Benitaka and BRS Isis), collected in the city of Petrolina, Pernambuco State, Northeast, Brazil.

In general, in all grape must samples, the K concentration was predominant, which varied between 718 and 1833 mg L^{-1}, followed by Ca and Mg concentrations. The grape must varieties "*Itália Melhorada*" and Benitaka were the samples that showed the highest concentration of K. Potassium had been the main metallic ion of grapes, and its excess interferes in fruit acidity, increasing the pH of must. Its deficiency, on the other hand, makes it difficult to transport carbohydrates formed in the leaves to other plant organs.[5]

The Ca concentrations found were between 45.9 and 115.6 mg L^{-1}, and the Arra-15 grape must sample showed the lowest concentration of this chemical element. This same sample showed a higher concentration of Mg, when compared to the concentrations of other varieties. The Mg values in all must samples varied between 35.5 and 122.4 mg L^{-1}.

The concentrations of Cu, Fe and Zn varied between 0.10-0.90, 0.50-6.10 and 0.06-3.03 mg L^{-1}, respectively. Must samples from Crimson, Benitaka and BRS Isis cultivars collected on the same farm showed higher Fe and Zn concentrations compared to other varieties. The presence of Mn competitively inhibits the absorption of Fe by grapevine. This may justify the higher concentrations of Fe in these samples, since it showed lower concentrations of Mn.[35]

The highest concentrations of Cu were found in Italy Moscato grape must, which varied between 0.36 and 3.03 mg L^{-1}, The Zn concentrations were similar to those of grapes from the south of Ukraine, while the Cu values were higher (Zn and Cu mean concentration were 0.37 and 0.05 mg L^{-1}, respectively).[13] The concentrations of Fe obtained in the analyzed samples were above the values found in the literature for grape pulp, which were around 0.60 mg L^{-1}.[35]

The varieties Italy Moscato, "*Itália Melhorada*", Crimson, Benitaka and BRS Isis presented higher Al concentrations than limit of quantification (LOQ = 0.60 mg L^{-1}) of the analytical method. Catarino *et al.*[18] quantified Al, Co, Cu, Cd and Pb in must and wine samples by graphite furnace atomic absorption spectrometry (GF AAS). The authors found an average concentration of Al equivalent to 2.40 mg L^{-1}, lower than the average value of 4.20 mg L^{-1} of Al from the proposed work. The concentration of Mn varied between 0.06 and 0.33 mg L^{-1}, similar to values found in the literature for Isabel grape must.[36] The samples Arra-15, Crimson, Benitaka and BRS Isis presented concentrations below than LOQ (< 0.03 mg L^{-1}) of the analytical method.

Regarding the chemical elements As and Se, only samples of must of the Arra-15 and Scarlotta grape varieties presented higher concentrations than LOQ of the proposed analytical method. The average concentration of As and Se was 0.19 and 0.47 mg L^{-1}, respectively. The sampling points located at the bottom and center of the cultivation area showed higher concentrations of Se, both in Arra-15 and Scarlotta grape samples.

Table 2. Concentration of Al, As, Ca, Cu, Fe, K, Mg, Mn, Se and Zn in the grape must samples collected in Petrolina, Pernambuco

Variety of grape must	Points	Al / (mg L^{-1})	As / (mg L^{-1})	Ca / (mg L^{-1})	Cu / (mg L^{-1})	Fe / (mg L^{-1})	K / (mg L^{-1})	Mg / (mg L^{-1})	Mn / (mg L^{-1})	Se / (mg L^{-1})	Zn / (mg L^{-1})
Italy Moscato	DFR	2.5 ± 0.5	< LOQ	81.2 ± 0.1	0.85 ± 0.03	1.5 ± 0.1	1013 ± 8	57.5 ± 0.8	0.100 ± 0.002	< LOQ	0.30 ± 0.03
	DFU	3.7 ± 0.2	< LOQ	109.9 ± 1.5	0.36 ± 0.02	1.2 ± 0.2	1471 ± 13	63.5 ± 0.6	0.28 ± 0.01	< LOQ	0.30 ± 0.02
	CEN	1.9 ± 0.1	< LOQ	50.9 ± 1.7	2.14 ± 0.03	1.4 ± 0.1	1211 ± 24	45.0 ± 1.6	0.180 ± 0.001	< LOQ	0.40 ± 0.05
	EFR	2.3 ± 0.2	< LOQ	66.8 ± 1.0	3.03 ± 0.05	1.8 ± 0.1	1078 ± 19	67.5 ± 2.0	0.22 ± 0.04	< LOQ	0.40 ± 0.01
	EFU	2.3 ± 0.3	< LOQ	53.9 ± 7.7	2.63 ± 0.4	1.6 ± 0.3	1010 ± 128	35.5 ± 7.8	0.19 ± 0.04	< LOQ	0.40 ± 0.05
"*Itália Melhorada*"	DFR	0.8 ± 0.2	< LOQ	54.0 ± 0.5	0.56 ± 0.02	1.14 ± 0.1	1640 ± 8	53.8 ± 0.8	< LOQ	< LOQ	0.10 ± 0.01
	DFU	< LOQ	< LOQ	85.5 ± 1.7	0.28 ± 0.002	0.95 ± 0.03	1451 ± 1	61.4 ± 1.8	0.22 ± 0.02	< LOQ	0.20 ± 0.01
	CEN	0.9 ± 0.1	< LOQ	46.4 ± 0.2	0.20 ± 0.02	1.03 ± 0.1	1608 ± 15	57.4 ± 1.7	0.15 ± 0.01	< LOQ	< LOQ
	EFR	0.9 ± 0.1	< LOQ	75.2 ± 1.3	0.07 ± 0.02	1.18 ± 0.2	1482 ± 39	56.6 ± 1.4	0.06 ± 0.01	< LOQ	< LOQ
	EFU	1.6 ± 0.1	< LOQ	80.6 ± 1.0	0.06 ± 0.01	0.88 ± 0.1	1556 ± 1	66.0 ± 0.4	0.32 ± 0.01	< LOQ	0.10 ± 0.01
Arra-15	DFR	< LOQ	0.51 ± 0.08	81.3 ± 0.2	0.18 ± 0.02	1.2 ± 0.1	1210 ± 9	122.4 ± 0.8	< LOQ	0.64 ± 0.07	0.10 ± 0.01
	DFU	< LOQ	0.300 ± 0.001	68.7 ± 0.4	0.16 ± 0.01	2.1 ± 0.04	1106 ± 3	115.8 ± 0.3	< LOQ	0.99 ± 0.05	< LOQ
	CEN	< LOQ	< LOQ	63.3 ± 0.5	0.28 ± 0.02	0.8 ± 0.1	1136 ± 9	111.8 ± 0.6	< LOQ	0.82 ± 0.05	0.30 ± 0.02
	EFR	< LOQ	0.30 ± 0.03	59.9 ± 0.03	0.13 ± 0.01	0.8 ± 0.1	1095 ± 9	104.2 ± 1.7	< LOQ	0.60 ± 0.11	< LOQ
	EFU	< LOQ	< LOQ	70.7 ± 0.5	0.17 ± 0.01	1.5 ± 0.1	1006 ± 3	115.9 ± 0.8	< LOQ	0.97 ± 0.21	< LOQ
Scarlotta	DFR	< LOQ	0.48 ± 0.03	107.9 ± 3.0	0.43 ± 0.03	1.1 ± 0.1	1091 ± 27	90.9 ± 1.4	0.15 ± 0.05	0.72 ± 0.01	0.10 ± 0.01
	DFU	< LOQ	0.30 ± 0.08	93.3 ± 1.3	0.35 ± 0.01	0.50 ± 0.04	1007 ± 4	85.2 ± 0.4	< LOQ	1.02 ± 0.28	< LOQ
	CEN	< LOQ	0.30 ± 0.05	89.8 ± 2.3	0.46 ± 0.02	0.7 ± 0.1	1117 ± 14	92.9 ± 0.2	0.13 ± 0.04	0.88 ± 0.07	0.20 ± 0.03
	EFR	< LOQ	< LOQ	90.3 ± 2.4	0.38 ± 0.01	0.8 ± 0.1	958 ± 13	82.7 ± 0.2	0.33 ± 0.04	0.79 ± 0.08	< LOQ
	EFU	< LOQ	0.48 ± 0.04	115.6 ± 3.3	0.28 ± 0.02	0.6 ± 0.1	1023 ± 15	96.6 ± 0.05	0.12 ± 0.02	0.93 ± 0.09	0.20 ± 0.03
Crimson	DFR	8.0 ± 0.7	< LOQ	92.1 ± 1.9	0.10 ± 0.02	4.1 ± 0.4	794 ± 56	61.8 ± 1.6	< LOQ	< LOQ	0.70 ± 0.01
	DFU	6.1 ± 0.7	< LOQ	99.5 ± 0.5	0.20 ± 0.01	4.7± 0.4	1078 ± 58	67.2 ± 0.6	< LOQ	< LOQ	0.7 ± 0.1
	CEN	5.0 ± 0.5	< LOQ	82.0 ± 1.8	0.20 ± 0.02	5.0± 0.3	1070 ± 122	59.1 ± 1.5	< LOQ	< LOQ	0.90 ± 0.02
	EFR	7.3 ± 0.8	< LOQ	45.9 ± 0.7	< LOQ	4.9± 0.4	1005 ± 104	56.7 ± 0.6	< LOQ	< LOQ	0.40 ± 0.01
	EFU	7.4 ± 0.5	< LOQ	84.6 ± 1.5	0.20 ± 0.02	4.8± 0.1	827 ± 3	56.5 ± 1.0	< LOQ	< LOQ	0.9 ± 0.1
Benitaka	DFR	6.6 ± 0.5	< LOQ	70.6 ± 0.6	< LOQ	4.1 ± 0.2	1385 ± 33	50.5 ± 2.0	< LOQ	< LOQ	0.20 ± 0.03
	DFU	5.1 ± 0.5	< LOQ	86.6 ± 0.3	0.07 ± 0.01	4.0 ± 0.1	1380 ± 27	52.5 ± 0.3	< LOQ	< LOQ	0.8 ± 0.1
	CEN	1.4 ± 0.4	< LOQ	93.1 ± 1.4	< LOQ	1.0 ± 0.2	1146 ± 34	49.4 ± 0.9	< LOQ	< LOQ	< LOQ
	EFR	8.3 ± 0.2	< LOQ	63.8 ± 0.9	0.06 ± 0.01	6.1 ± 0.1	1833 ± 4	52.9 ± 1.0	< LOQ	< LOQ	0.8 ± 0.1
	EFU	8.4 ± 0.6	< LOQ	51.6 ± 0.7	0.10 ± 0.01	5.2 ± 0.5	1392 ± 33	48.0 ± 1.1	< LOQ	< LOQ	0.5 ± 0.1
BRS Isis	DFR	5.8 ± 0.5	< LOQ	115.5 ± 4.7	< LOQ	4.4 ± 0.2	1105 ± 60	50.1 ± 1.3	< LOQ	< LOQ	0.50 ± 0.01
	DFU	3.3 ± 0.5	< LOQ	73.1 ± 1.0	< LOQ	3.7 ± 0.4	1059 ± 56	51.6 ± 0.6	< LOQ	< LOQ	0.100 ± 0.005
	CEN	2.5 ± 0.4	< LOQ	73.0 ± 0.05	< LOQ	3.3 ± 0.4	1055 ± 34	48.6 ± 0.1	< LOQ	< LOQ	0.40 ± 0.03
	EFR	4.6 ± 0.2	< LOQ	109.8 ± 1.2	< LOQ	3.9 ± 0.3	1045 ± 61	54.9 ± 1.2	< LOQ	< LOQ	0.10 ± 0.04
	EFU	4.0 ± 0.6	< LOQ	85.8 ± 1.6	< LOQ	3.6 ± 0.3	718 ± 48	50.9 ± 0.6	< LOQ	< LOQ	0.30 ± 0.09
Average		4.2	0.33	79.2	0.52	2.4	1176	68.4	0.19	0.84	0.3
Median		3.9	0.30	81.2	0.20	1.5	1095	57.5	0.18	0.85	0.2
RSD / %		5.5	7.0	3.6	6.1	4.0	3.9	2.7	4.0	4.6	3.8
Minimum		0.8	0.15	45.9	0.06	0.5	718	35.5	0.06	0.60	0.1
Maximum		8.4	0.51	115.6	3.03	6.1	1833	122.4	0.33	1.02	0.9
Brazilian Food Composition Table (TACO)[37] / (mg L^{-1})		–	–	74.0	1.2	1.06	1712	52.8	1.4	–	Tr

Results expressed as mean ± 95% confidence interval; LOQ: less than the limit quantification; Tr: trace; RSD: relative standard deviation; DFR: front right; DFU: bottom right; CEN: center; EFR: front left; EFU: bottom left.

The degree of difference in the concentration of Al, Ca, Cu, Fe, K and Mg in the our study and those found in the literature can be related depending on the grape varieties, the type of cultivation, climatic conditions, type of soil, use of different types of fertilizer and fungicides, proximity of vines to industries and highways, among others.[35] The samples of grape must Italy Moscato and "*Itália Melhorada*" were the ones that showed higher concentrations of Cu and K, which may be related to the type of soil in the cultivation area, close to a highway and/or use of Cu-based fungicides for a long time and/or above permitted doses.

According to the Brazilian Food Composition Table (Tabela Brasileira de Composição de Alimentos, TACO),[37]

the chemical composition of the edible part (skinless grape) of Italy grape *per* 100 g was 7.0 mg for Ca; 0.11 mg for Cu; 0.10 mg for Fe; 162 mg for K; 5 mg for Mg; 0.13 mg for Mn and traces for Zn. In this study, there was no significant difference ($p > 0.05$) between the average concentrations of the elements obtained and the values presented in the TACO, applying the *t* test, at the 95% confidence level. No information was found on TACO for Al, As and Se concentrations.[37]

The Brazilian Health Surveillance Agency (Agência Nacional de Vigilância Sanitária, Anvisa)[38] determines the maximum tolerance limit (LMT) of inorganic contaminants in food, Cu of 10.0 mg kg^{-1} and As of 0.30 mg kg^{-1}.[38] In this work, it can be seen that the concentrations found for Cu are below the maximum tolerance limit. However, the concentration ranges of As in the Arra-15 and Scarlotta grape must samples it is noted that two points of the Scarlotta variety (DFR and EFU) and one point of the sample of the cultivar Arra-15 (DFR) presented values above the maximum allowed limit, according to Anvisa.[38]

The mobility and different levels of toxicity of As are associated with changes in the oxidation state (As^{5+} and As^{3+}). The oxidation status of As^{3+} over prolonged periods can cause health risks.[39] Therefore, it is recommended that complementary study be carried out aiming to evaluate the concentrations of As and Se, through analysis by chemical speciation and an evaluation of bioaccessibility in the grape must samples Arra-15 and Scarlotta.

Multivariate data analysis generated from grape must analysis

The profile of the different types of grapes produced in the region Submedium São Francisco was established using PCA. The data were pre-processed through autoscaling. For PCA, the matrix was constructed with 10 variables using concentration of Al, As, Ca, Cu, Fe, K, Mg, Mn, Se and Zn, as columns, and 35 samples analyzed, as lines. The data generated by first three principal components synthesized an accumulated variance around 72% of the cases, explaining the original data set.

The characterization of the trends of the variables was evaluated by loadings graph shown in Figure 1a. Figure 1b shows the distribution of the grape must samples. It is noticed that the variations of the concentration of the analytes in the samples influenced the separation of five groups on the three main components.

In the first group, the greatest positive loadings in the first principal component (PC1: 39.5%) are the variables linked to the concentrations of Se, As and Mg, which influence the samples of grape must Arra-15 and Scarlotta
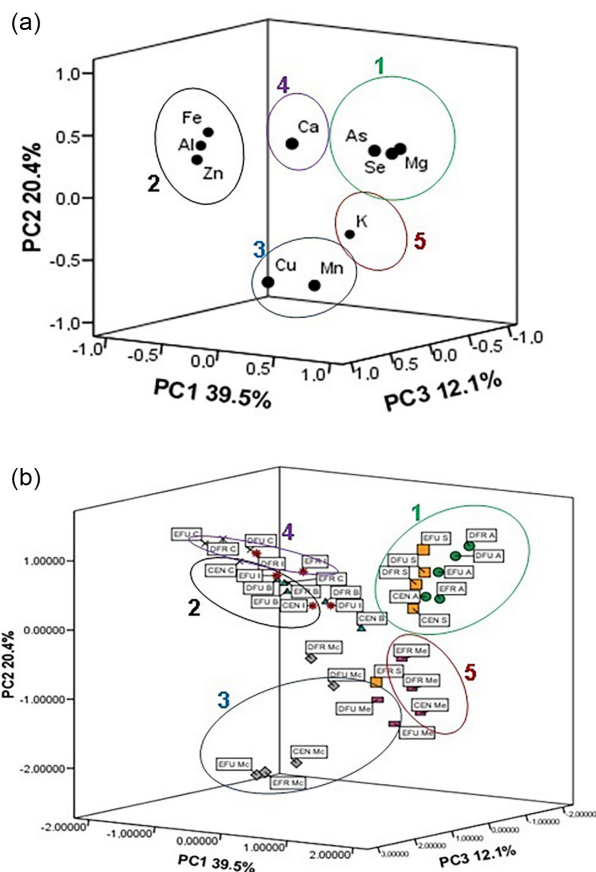

Figure 1. (a) Loadings graph for the first three principal components. (b) Three-dimensional graph of scores for PC3 × PC2 × PC1 related to grape must samples Italy Moscato, "*Itália Melhorada*", Arra-15, Scarlotta, Crimson, Benitaka and BRS Isis. Italy Moscato grape (◆), "*Itália Melhorada*" grape (■), Arra-15 grape (●), Scarlotta grape (■), Crimson grape (✕), Benitaka grape (▲) and BRS Isis grape (★).

that belong to the same cultivation farm. The greatest negative loadings were observed in the concentrations of Al, Fe and Zn, governed by majority of the Crimson, Benitaka samples and a BRS Isis sample, that belong to the same farm, contained in the second group. Along the PC2 axis (negative loadings) with 20.4% of the total variance, the variables that contribute the most in the third group were the samples of grape must with Italy Moscato seed that present higher concentrations of Cu and Mn, in most of the points. The concentration of Ca influences the clustering of most of the BRS Isis and one Crimson samples, which showed positive scores values for PC2. Finally, the fifth group was influenced by negative loading values on the PC3 axis (12.1% of the total variance) from K concentration, formed by almost all samples of "*Itália Melhorada*" grape must.

According to Pearson's correlation between the ten variables considered in this study, the highest correlations occur between the variables Fe-Al ($r = 0.927$), Zn-Al ($r = 0.755$), Zn-Fe ($r = 0.744$), Mg-As ($r = 0.639$), Mg-Se ($r = 0.844$) and Se-As ($r = 0.561$), which may indicate a

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great interconnection of Al with Fe and Zn, and Fe with Zn in the grape musts under study. The concentrations of Fe and Zn were naturally present in small amounts in the grapes. In addition, the concentration of Mg has a great interaction with the concentrations of As and Se in the samples. There was also a relatively important correlation between the pairs Mg-Al (r = −0.542), Se-Al (r = −0.552) and Fe-Mn (r = −0.504), and this negative correlation indicates a decrease in the availability of chemical element

with an increase in the other element, for example, Mn inhibits the absorption of Fe by the vine.[35]

Determination and evaluation of essential and potentially toxic elements in soil

The results obtained from the average concentrations for determination of the elements Cu, Mn, Pb, Zn, Co, Ni, V and Fe in soil samples are shown in Table 3. Al, As, Ca,

Table 3. Concentration of Pb, Co, Cu, Fe, Mn, Ni, V and Zn in soil samples from Italy Moscato grape cultivation, "*Itália Melhorada*" , Arra-15, Scarlotta, Crimson, Benitaka and BRS Isis collected in Petrolina, Pernambuco

Soil	Points	Pb / (µg g⁻¹)	Co / (µg g⁻¹)	Cu / (µg g⁻¹)	Fe / %	Mn / (µg g⁻¹)	Ni / (µg g⁻¹)	V / (µg g⁻¹)	Zn / (µg g⁻¹)
Italy Moscato	DFR	15.3 ± 0.4	9.7 ± 0.7	53.5 ± 2.1	0.696 ± 0.001	199.0 ± 12.5	19.1 ± 3.8	30.6 ± 0.3	134.7 ± 7.6
	DFU	14.8 ± 0.8	10.9 ± 0.5	59.8 ± 5.6	1.09 ± 0.06	230.0 ± 16.5	37.1 ± 2.6	34.7 ± 0.5	126.1 ± 12.6
	CEN	15.6 ± 1.2	10.0 ± 0.1	63.7 ± 1.9	0.83 ± 0.03	231.0 ± 7.5	21.0 ± 1.4	29.3 ± 0.7	131.4 ± 6.3
	EFR	14.1 ± 0.9	10.8 ± 0.5	63.7 ± 3.8	1.05 ± 0.03	293 ± 23	24.3 ± 0.7	31.7 ± 1.6	154.3 ± 4.8
	EFU	20.7 ± 2.7	30.1 ± 4.9	69.4 ± 0.9	1.81 ± 0.09	650 ± 90	56.7 ± 1.5	25.5 ± 4.5	114.7 ± 6.6
"*Itália Melhorada*"	DFR	15.2 ± 1.1	11.2 ± 0.7	38.5 ± 1.5	0.84 ± 0.05	130.0 ± 2.1	17.7 ± 1.4	32.1 ± 0.7	82.3 ± 1.7
	DFU	16.3 ± 1.1	10.4 ± 0.9	39.0 ± 0.7	0.70 ± 0.02	125.0 ± 2.6	16.6 ± 0.04	28.3 ± 0.6	72.8 ± 1.8
	CEN	17.3 ± 1.3	11.0 ± 0.3	48.7 ± 0.9	1.13 ± 0.04	166 ± 13	21.2 ± 0.5	36.9 ± 1.5	102 ± 2.3
	EFR	< LOQ	< LOQ	24.5 ± 0.5	1.29 ± 0.04	151.0 ± 8.4	10.3 ± 1.1	31.6 ± 4.6	68.5 ± 3.4
	EFU	< LOQ	< LOQ	26.0 ± 1.2	0.82 ± 0.02	162.0 ± 7.8	8.8 ± 1.5	18.8 ± 2.7	71.5 ± 2.3
Arra-15	DFR	< LOQ	< LOQ	10.0 ± 1.5	0.28 ± 0.03	101.2 ± 9.4	15.4 ± 2.7	6.8 ± 0.1	26.3 ± 4.1
	DFU	< LOQ	< LOQ	16.9 ± 1.3	0.51 ± 0.02	156.9 ± 8.3	31.9 ± 2.5	7.7 ± 0.8	40.2 ± 1.9
	CEN	< LOQ	< LOQ	22.4 ± 2.5	0.32 ± 0.01	136.5 ± 7.0	25.2 ± 1.8	6.1 ± 0.4	47.7 ± 3.3
	EFR	< LOQ	< LOQ	20.9 ± 0.7	0.37 ± 0.03	183.0 ± 0.05	25.8 ± 1.2	8.0 ± 1.2	48.5 ± 1.2
	EFU	< LOQ	< LOQ	9.1 ± 0.5	0.47 ± 0.1	74.7 ± 5.6	28.1 ± 1.4	6.4 ± 0.6	20.7 ± 4.2
Scarlotta	DFR	< LOQ	< LOQ	10.1 ± 1.4	0.90 ± 0.02	335.4 ± 6.3	7.8 ± 0.9	16.3 ± 0.8	62.6 ± 2.3
	DFU	< LOQ	< LOQ	19.6 ± 2.6	0.55 ± 0.04	117.5 ± 13.2	65.3 ± 3.9	12.2 ± 1.5	14.5 ± 2.5
	CEN	< LOQ	< LOQ	3.4 ± 0.8	0.71 ± 0.02	129.3 ± 4.4	12.5 ± 1.0	13.1 ± 0.2	19.5 ± 2.4
	EFR	< LOQ	< LOQ	2.2 ± 0.6	0.60 ± 0.03	173.8 ± 7.8	3.3 ± 0.5	10.8 ± 0.7	22.9 ± 3.4
	EFU	< LOQ	< LOQ	13.0 ± 0.4	0.72 ± 0.01	203.9 ± 12.7	32.1 ± 1.1	14.2 ± 0.6	40.5 ± 3.8
Crimson	DFR	4.3 ± 0.3	2.1 ± 0.1	11.5 ± 1.0	0.51 ± 0.04	90.7 ± 5.1	5.1 ± 0.1	12.9 ± 1.4	34.6 ± 0.3
	DFU	3.2 ± 0.1	1.7 ± 0.2	10.2 ± 0.6	0.56 ± 0.04	79.6 ± 3.3	5.4 ± 0.6	13.0 ± 0.7	31.8 ± 2.3
	CEN	5.3 ± 1.0	1.6 ± 0.2	10.9 ± 0.6	0.51 ± 0.02	79.7 ± 4.2	4.2 ± 0.4	11.3 ± 0.2	29.4 ± 1.0
	EFR	3.8 ± 0.9	1.5 ± 0.1	12.0 ± 0.4	0.501 ± 0.005	92.7 ± 2.3	4.3 ± 0.04	12.0 ± 0.3	33.4 ± 1.4
	EFU	3.2 ± 0.2	1.1 ± 0.3	7.8 ± 0.6	0.45 ± 0.02	69.8 ± 2.8	3.8 ± 0.1	11.8 ± 0.8	24.6 ± 0.1
Benitaka	DFR	3.3 ± 0.7	1.4 ± 0.2	11.8 ± 0.4	0.45 ± 0.02	54.3 ± 3.4	3.5 ± 1.2	11.2 ± 0.1	20.3 ± 1.3
	DFU	7.3 ± 1.1	3.0 ± 0.3	20.3 ± 0.6	0.89 ± 0.04	129.5 ± 3.0	8.5 ± 0.5	17.8 ± 0.1	45.9 ± 0.3
	CEN	3.9 ± 0.9	0.9 ± 0.2	10.6 ± 0.9	0.440 ± 0.003	50.8 ± 6.3	2.7 ± 0.5	11.9 ± 0.4	36.0 ± 3.3
	EFR	3.2 ± 0.3	1.5 ± 0.3	11.7 ± 0.5	0.56 ± 0.03	64.0 ± 2.8	3.9 ± 0.2	12.3 ± 0.6	23.1 ± 0.8
	EFU	5.4 ± 0.6	2.6 ± 0.2	13.3 ± 1.3	0.812 ± 0.002	81.5 ± 7.3	6.2 ± 0.2	16.5 ± 0.5	29.4 ± 2.2
BRS Isis	DFR	< LOQ	1.1 ± 0.3	10.8 ± 0.3	0.45 ± 0.02	83.4 ± 1.4	4.4 ± 0.1	11.3 ± 0.2	25.4 ± 1.1
	DFU	4.5 ± 0.4	1.7 ± 0.1	9.7 ± 0.7	0.65 ± 0.04	61.1 ± 6.5	5.3 ± 0.3	13.9 ± 1.2	24.6 ± 2.2
	CEN	4.4 ± 0.3	1.5 ± 0.2	8.6 ± 0.6	0.61 ± 0.04	72.1 ± 3.2	5.2 ± 0.4	14.3 ± 1.2	21.1 ± 1.3
	EFR	4.6 ± 0.2	1.6 ± 0.1	11.3 ± 0.3	0.62 ± 0.02	77.7 ± 1.7	5.4 ± 0.2	14.6 ± 0.5	27.4 ± 1.1
	EFU	3.6 ± 0.2	1.6 ± 0.2	8.7 ± 0.7	0.67 ± 0.02	65.3 ± 4.1	6.2 ± 0.3	14.9 ± 0.4	23.9 ± 2.0
Average		8.1	5.6	22.4	0.70	145.8	15.8	17.2	52.5
Median		4.6	1.7	12.0	0.62	125.0	8.8	13.9	34.6
RSD / %		7.8	4.6	5.0	8.6	5.5	5.8	6.2	3.7
Minimum		1.4	0.9	2.2	0.28	50.8	2.7	6.1	14.5
Maximum		20.7	30.1	69.4	1.81	650.0	65.3	36.9	154.3
CONAMA (quality reference values)[29]		13.0	4.0	5.0	–	–	9.0	24.0	35.0

Results expressed as mean ± 95% confidence interval; LOQ: less than the limit of quantification; RSD: relative standard deviation; DFR: front right; DFU: bottom right; CEN: center; EFR: front left; EFU: bottom left.

K, Mg and Se were also determined in the soil samples, but no values considered satisfactory were obtained when compared to the certified values obtained using the CRM of the San Joaquin soil (NIST 2709a).

The National Council for the Environment (CONAMA) through Resolution No. 420/2009 proposes values that guide the quality of the soil in terms of the presence of essential and potentially toxic elements.[29] The values are established in quality reference values (QRVs), prevention (VP) and investigation (VI). Since the QRVs are established from statistical interpretation of the results obtained in samples collected in the main types of soil in the Pernambuco state, Northeast, Brazil, it defines the natural quality of the soil. The VP had been the limit concentration of a given substance in the soil and the VI had been the concentration with potential risks, direct or indirect, to human health.[40] The QRVs of the state of Pernambuco are established by Normative Instruction on State Environmental Agency of the Pernambuco State (Agência Estadual de Meio Ambiente do Estado de Pernambuco, CPRH) No. 7 of 07/07/2014.[40]

Thus, if the metals concentrations present in the soil are equal to or less than the QRVs, it is not considered as contaminated. Based on this, it is observed that all soil samples had values lower than 72 μg g^{-1} of Pb, which is below the defined limit of prevention (VP). Lead concentrations ranged from 3.2 to 20.7 μg g^{-1} and only the soils of Moscato cultivation and three samples of "*Itália Melhorada*" cultivation showed higher values than the QRV for this element.

The mobility of Pb in the soil for the fruit (grape) had been very slow under natural conditions, since lead carbonates ($PbCO_3$ and $Pb_2(OH)_2CO_3$) are formed and retained in the soil at pH above 5.4.[41] This explains the concentrations of this toxic metal found in soil samples, whereas in grape must the concentration values for Pb were below the LOQ for all samples. Thus, pH can determine the availability of species in the soil through acid-base equilibrium.[42]

The Moscato and "*Itália Melhorada*" soil cultivation samples showed Co concentrations with values higher than the QRV established in Pernambuco soils, which ranged from 0.9 to 30.1 μg g^{-1}. In addition, the EFU point of the Moscato samples showed a value higher than the permitted limit concentration of Co in the soil.

Copper concentrations in soils ranged from 2.2 to 69.4 μg g^{-1}. Only two samples (CEN and EFR) of Scarlotta grape cultivation showed values lower than the QRV for Cu. The other samples had concentrations higher than QRV and lower than VP. Only three soil samples from the center and left side of the Moscato cultivation area (CEN, EFR and EFU) were above the limit concentration for Cu.

The high concentrations of Cu in the analyzed soils may be associated with cupric treatments used to protect vines against fungal diseases, if applied in doses above those recommended.

The results for Crimson, Benitaka, BRS Isis grape cultivation soil samples, two points located in front of the study area for the Scarlotta grape cultivation and one more point for the "*Itália Melhorada*" (EFU) cultivation showed Ni concentrations lower than the QRV of Pernambuco State, Northeast, Brazil. The soils collected at the bottom of the areas of two Moscato samples (DFU and EFU), one Arra-15 (DFU) and two Scarlotta (DFU and EFU) obtained results that exceeded the allowed value for Ni concentration (2.7 to 65.3 μg g^{-1}), but still lower than the intervention values. Most soil samples that presented concentrations higher than VP, had a pH greater than 6.7, and, at this value, the solubility of Ni is limited by the presence of hydroxides, phosphates and carbonates, that is, its availability is inversely related to the pH of the environment.[25]

The results obtained for V concentrations showed a variation of 6.4 and 36.9 μg g^{-1}, with values lower than the QRV for most of the studied samples. Only samples of cultivated soil from Italy Moscato and one cultivar of "*Itália Melhorada*" had higher concentrations than the QRV. All soil samples analyzed showed results below the permitted limit of prevention for Zn, ranging from 14.5 to 154.3 μg g^{-1}. In addition, all samples from Crimson, Benitaka, BRS Isis, plus two Arra-15 sample points (DFR and EFU) and three Scarlotta sample points (DFU, CEN and EFR) obtained concentration below QRV for this chemical element.

Since the Resolution No. 420/2009 of the CONAMA and CPRH Normative No. 7 of 07/07/2014, values of QRV, VP and VI are not stipulated for the concentrations of Mn and Fe, since these are usually naturally found in high concentrations in the soil.[29,40] Thus, according to results presented in Table 3, it was possible to visualize that the samples of grape cultivation soil Italy Moscato and "*Itália Melhorada*" were the ones that presented the highest concentration results for most of the studied elements, with no sample exceeding the value stipulated for an intervention in agricultural soils based on the aforementioned resolution.[29]

According to this resolution,[29] samples of cultivated soil from "*Itália Melhorada*", Crimson, Benitaka and BRS Isis presented higher concentrations of at least one chemical element than the QRV and less than or equal to VP, being considered class 2. Soils of class 2 require an assessment by an environmental agency to verify the possibility of the substance being from a natural or anthropic source. Samples of cultivated soil from Italy Moscato showed concentrations

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of Co, Cu and Ni, and soil samples of Arra-15 and Scarlotta showed higher concentrations of Ni than VP, and less than or equal to VI, being classified as class 3. On the other hand, class 3 soils require assessment of the natural occurrence of the substance, identification and control of sources of contamination, as well as monitoring of soil quality.

Considering that changes in pH have an influence on the availability of chemical elements for grapevine/grape, pH values were measured for all grape cultivation soils under study. The averages of the pH values ranged from moderately acidic (6.0 in soil of cultivation of Benitaka grapes and BRS Isis) to slightly neutral (7.4 in soil of cultivation of grape Arra-15). In the Scarlotta grape soil there was greater variation over the cultivation area, with the soil tending to moderate basic (6.4 to 7.8). The availability of elements in the soil is relatively low at pH values around 6.5 to 7.[43]

According to Lemiska,[44] the excess of Al in acidic soil results in the low development of the root system of plants and consequently less exploration of soil volume, which reduces the absorption of nutrients, such as Ca and Mg. Thus, the slightly alkaline pH in the soil inhibits the solubilization of exchangeable aluminum (Al concentration was below than LOQ) and contributes to higher Mg concentrations in Arra-15 and Scarlotta grape must samples. These samples were also the only ones with higher concentration values of Se than LOQ (0.4 mg L^{-1}), which agrees with the negative correlation of Mg and Se with Al, as previously discussed in Pearson's correlation analysis of grape samples.

Geochemical basis and pollution index values

The limit values established by guide quality values of soil contribute to guide the analysis of the study area. However, other criteria need to be associated, since variations in the concentration of chemical elements in the soil depend on several factors, as previously discussed. In view of this, the soils of the study area may have background levels higher than values of the quality guides.[8] In this work, Fe concentration was chosen as a normalization element because it is the second most abundant metal on Earth, and it is present in very insoluble compounds (oxidhydroxides) in aerobic environments.[9]

In Pearson's correlation analysis with a 95% confidence level (significance level of $p = 0.05$), significant correlations (> 0.50) were found between Fe and chemical elements, which may indicate an important interconnection. The positive correlations between Fe and the other chemical elements may indicate that a change in the concentration of the normalizing element (Fe) will change proportionally

to the concentration of the chemical elements (Cu, Co, Mn, Zn, Pb and V).

The enrichment factor (EF) has been used mainly to estimate the effects of human activities on soil contamination. Table 4 shows the EF values calculated for the elements at each collection point in the vine cultivation areas under study.

Table 4. Values of enrichment factor (EF) calculated for each point of collection of soil samples of vine cultivation in Petrolina, Pernambuco state, Northeast, Brazil

Point	Cu	Co	Mn	Zn	Ni	Pb	V
DFR Mc	4.1	2.3	2.2	4.2	2.0	2.8	2.5
DFU Mc	1.7	0.7	1.3	1.6	1.1	1.0	1.5
CEN Mc	3.5	1.4	2.1	3.1	1.4	2.1	2.0
EFR Mc	2.3	0.8	2.0	2.5	0.9	1.2	1.7
EFU Mc	1.3	1.1	2.9	1.1	1.1	0.9	0.9
DFR Me	1.5	1.1	0.8	1.4	0.8	1.4	1.6
DFU Me	2.3	1.9	1.1	1.8	1.3	2.3	1.8
CEN Me	1.1	0.5	0.7	1.0	0.5	0.9	1.2
EFR Me	0.4	n.d.	0.5	0.5	0.2	n.d.	0.8
EFU Me	1.2	n.d.	1.2	1.4	0.5	n.d.	1.1
DFR A	18.4	n.d.	3.7	5.0	−6.6	n.d.	1.6
DFU A	2.6	n.d.	2.6	2.2	10.7	n.d.	0.9
CEN A	16.7	n.d.	4.5	6.9	−16.7	n.d.	1.3
EFR A	10.1	n.d.	5.6	5.9	−40.7	n.d.	1.6
EFU A	1.3	n.d.	1.1	1.0	12.5	n.d.	0.6
DFR S	0.6	n.d.	3.3	1.6	0.5	n.d.	1.2
DFU S	2.1	n.d.	1.5	0.6	12.8	n.d.	1.1
CEN S	0.2	n.d.	1.1	0.5	1.0	n.d.	0.8
EFR S	0.2	n.d.	2.4	0.9	0.6	n.d.	1.0
EFU S	0.9	n.d.	2.2	1.2	3.1	n.d.	1.1
DFR C	1.4	2.0	1.2	1.5	1.4	1.3	1.2
DFU C	0.9	0.7	0.9	1.1	0.9	0.7	1.0
CEN C	1.3	1.4	1.0	1.2	1.0	1.5	1.0
EFR C	1.6	1.8	1.3	1.5	1.3	1.2	1.1
EFU C	1.3	−9.4	1.1	1.3	2.5	1.3	1.2
DFR B	1.8	−8.5	0.8	1.0	2.2	1.3	1.1
DFU B	0.7	0.2	0.8	0.7	0.3	0.6	0.8
CEN B	1.7	−2.8	0.7	1.8	2.1	1.6	1.1
EFR B	1.0	0.7	0.7	0.7	0.6	0.7	0.9
EFU B	0.5	0.2	0.5	0.4	0.3	0.5	0.7
DFR I	1.9	−10.0	1.3	1.4	3.1	n.d.	1.2
DFU I	0.6	0.3	0.5	0.6	0.4	0.6	0.8
CEN I	0.6	0.4	0.7	0.6	0.6	0.8	0.9
EFR I	0.8	0.4	0.7	0.7	0.6	0.8	0.9
EFU I	0.5	0.3	0.5	0.5	0.5	0.5	0.8

n.d.: not determined; DFR: front right; DFU: bottom right; CEN: center; EFR: front left; EFU: bottom left; Mc: Italy Moscato; Me: "*Itália Melhorada*"; A: Arra-15; S: Scarlotta; C: Crimson; B: Benitaka; I: BRS Isis.

According to the classification proposed by Hakanson,[31] most soil samples were classified with minimum enrichment levels in relation to the concentration of Cu, Co, Mn, Zn, Ni, Pb and V, since they presented EF < 2. These results showed that, in these samples, these chemical elements can be considered as coming from natural processes.

For Cu concentration, a sample of cultivated soil from "*Itália Melhorada*" (DFU), one from Arra-15 (DFU) and one from Scarlotta (DFU) presented EF values classified as moderate enrichment level, (2.3), (2.6) and (2.1), respectively. The EF values for Cu, Mn, Zn and Pb concentrations at most of the sampling points of the Moscato grape cultivation soil samples were between 2 and 5, that is, they also present a moderate level of enrichment. Most Arra-15 and Scarlotta soil samples showed moderate enrichment for Mn concentration. The EF values found in most Benitaka soil samples and a BRS Isis soil sample (DFR) indicated moderate enrichment for Ni. Finally, only a sample of Moscato DRF soil had moderate enrichment for the concentration found for V. These results show that the concentrations of these chemical elements were due to anthropic activities.

The Arra-15 soil samples called DFR, CEN and EFR, showed EF values between 5 and 20 in relation to the concentration of Cu and Zn, therefore, they were classified as significant enrichment. A sample of the Arra-15 grape (EFR) also showed a significant enrichment level, equal to 5.6 in relation to the Mn concentration. For the concentrations of Ni found, two samples of Arra-15 soil (DFU and EFU) and a Scarlotta sample (DFU) presented EF values equal to (10.7); (12.5) and (12.8), respectively, being also classified with significant enrichment. It was observed that no sample showed high levels of enrichment and EF values greater than 20. Similarly, using equation 2 and the estimated background values, geoaccumulation indexes (I_{geo}) were calculated for each soil collection point as shown in Table 5. The I_{geo} value is used to study the degree of contamination.

According to classification proposed by Müller,[32] the values of $I_{geo} < 0$ indicated practically unpolluted cultivation areas, therefore, analyzing the results, most samples from the analyzed areas are considered to be practically non-polluted. However, two soil samples of Italy Moscato soil (DFR and CEN) and one sample of Arra-15 soil (EFR) obtained I_{geo} values that varied between 1.14 to 1.71 for Cu concentration, indicated moderate level of contamination (class 2). DFR samples from Italy Moscato and CEN from Arra-15 soil also belong to class 2 in relation to Zn concentration, with I_{geo} values equal to 1.29 and 1.19, respectively.

Five samples showed moderate to strong contamination level, according to Müller's classification.[32] Two soil

Table 5. Values of geoaccumulation index (I_{geo}) calculated for each point of collection of soil samples from vine cultivation in Pernambuco state, Northeast, Brazil

Point	Cu	Co	Mn	Zn	Ni	Pb	V
DFR Mc	1.25	0.41	0.39	1.29	0.21	0.73	0.54
DFU Mc	0.51	–0.83	0.09	0.47	–0.07	–0.24	0.32
CEN Mc	1.14	–0.17	0.42	0.97	–0.19	0.39	0.33
EFR Mc	0.66	–0.76	0.48	0.81	–0.60	–0.24	0.22
EFU Mc	–0.16	–0.46	0.97	–0.46	–0.50	–0.65	–0.66
DFR Me	0.37	–0.08	–0.44	0.26	–0.50	0.31	0.44
DFU Me	0.77	0.46	–0.30	0.38	–0.04	0.79	0.42
CEN Me	0.14	–0.91	–0.42	0.10	–0.97	–0.09	0.37
EFR Me	–1.08	n.d.	–0.71	–0.67	–2.28	n.d.	0.02
EFU Me	–0.14	n.d.	–0.09	0.10	–1.43	n.d.	–0.30
DFR A	2.55	n.d.	0.25	0.67	n.d.	n.d.	–1.02
DFU A	0.33	n.d.	0.35	0.07	2.38	n.d.	–1.21
CEN A	2.46	n.d.	0.56	1.19	n.d.	n.d.	–1.26
EFR A	1.71	n.d.	0.87	0.94	n.d.	n.d.	–0.94
EFU A	–0.32	n.d.	–0.64	–0.73	2.91	n.d.	–1.42
DFR S	–1.69	n.d.	0.86	–0.23	–1.85	n.d.	–0.59
DFU S	0.34	n.d.	–0.14	–1.54	2.94	n.d.	–0.61
CEN S	–2.76	n.d.	–0.25	–1.52	–0.46	n.d.	–0.70
EFR S	–3.01	n.d.	0.35	–1.01	–1.74	n.d.	–0.84
EFU S	–0.86	n.d.	0.39	–0.49	0.86	n.d.	–0.59
DFR C	–0.22	0.30	–0.44	–0.14	–0.26	–0.32	–0.47
DFU C	–0.64	–0.94	–0.72	–0.43	–0.73	–1.01	–0.53
CEN C	–0.31	–0.15	–0.63	–0.39	–0.57	–0.04	–0.66
EFR C	–0.10	0.11	–0.39	–0.16	–0.35	–0.44	–0.56
EFU C	–0.41	n.d.	–0.70	–0.40	0.55	–0.35	–0.51
DFR B	0.20	n.d.	–1.05	–0.67	0.49	–0.30	–0.58
DFU B	–0.67	–2.14	–0.51	–0.67	–1.71	–0.87	–0.46
CEN B	0.11	n.d.	–1.13	0.19	0.43	0.01	–0.48
EFR B	–0.42	–1.04	–1.03	–0.88	–1.16	–0.99	–0.60
EFU B	–1.09	–2.07	–1.07	–1.16	–1.90	–1.11	–0.48
DFR I	0.06	n.d.	–0.44	–0.36	0.77	n.d.	–0.57
DFU I	–1.05	–1.81	–1.24	–1.04	–1.38	–0.86	–0.54
CEN I	–1.07	–1.60	–0.94	–1.15	–1.15	–0.74	–0.45
EFR I	–0.74	–1.68	–0.86	–0.82	–1.20	–0.74	–0.44
EFU I	–1.30	–2.03	–1.19	–1.15	–1.31	–1.28	–0.47

n.d.: not determined; DFR: front right; DFU: bottom right; CEN: center; EFR: front left; EFU: bottom left; Mc: Italy Moscato; Me: "*Itália Melhorada*"; A: Arra-15; S: Scarlotta; C: Crimson; B: Benitaka; I: BRS Isis.

samples belong to points located at the bottom of the Arra-15 cultivation area (DFU and EFU) and a Scarlotta soil sample (DFU) in relation for Ni concentration with values of 2.4, 2.9 and 2.9, respectively. The other two samples that were classified as class 3, with I_{geo} values equal to 2.5 are from Arra-15 cultivation soil (DFR and CEN) for Cu.

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Therefore, according to the results obtained through the calculated values of EF and I_{geo}, the same points of possible significant enrichment and moderate to strong contamination were found, with some exceptions, for the concentrations of Ni and Cu. Thus, for the assessment of ecological risk of essential and potentially toxic elements, it is important for a better investigation to be carried out in relation for Ni and Cu concentrations.

Strong and positive correlations were found between the chemical elements, which may indicate that it was from the same source and may have been derived from anthropic sources. In addition, it was worth noting that the results found are preliminary, since 3 samples from each 7 vine cultivation areas were used to construct the linear regression analysis with the objective of finding the background values.

The analysis of the results showed that establishing a regional geochemical base of the vine cultivation areas in the city of Petrolina, Permanbuco state, Northeast, Brazil was the most appropriate, since it probably leads to lesser mistakes in interpretation when compared to works that use the global geochemical base. As previously mentioned, soil formation comes from several natural and man-made sources, which makes it difficult to compare the results found in the various works developed in Brazil and in other countries. In addition, calculated values of EF and I_{geo} contributed to the classification in relation to the level of contamination of the area. In general, this study is a pioneer in carrying out a preliminary analysis on the construction of a regional geochemical base that provides basic data for future work.

Multivariate data analysis for grape cultivation soil samples

The data matrix for PCA was constructed using 9 variables as columns (concentrations of Cu, Co, Pb, Zn, V, Fe, Mn, Ni and pH) and 35 soil samples as lines. The data were pre-processed through autoscaling. The first two principal components explained of variance about 81.8% of the total variance data, explaining the original data set, with PC1 representing 64.0% and PC2 accounting for 17.8% of the total variance.

Examining the loadings and score graphs illustrated in Figures 2a and 2b, respectively, it was possible to observe the agglomeration of three groups, based on the chemical composition of the analyzed samples. The first group was formed by samples of cultivated soil from the grapes Italy Moscato and from "*Itália Melhorada*", which presented the highest positive weights in PC1 for the concentrations of Cu, Co, Fe, Mn, Pb, V and Zn. It is important to note that these samples had high concentrations of these chemical

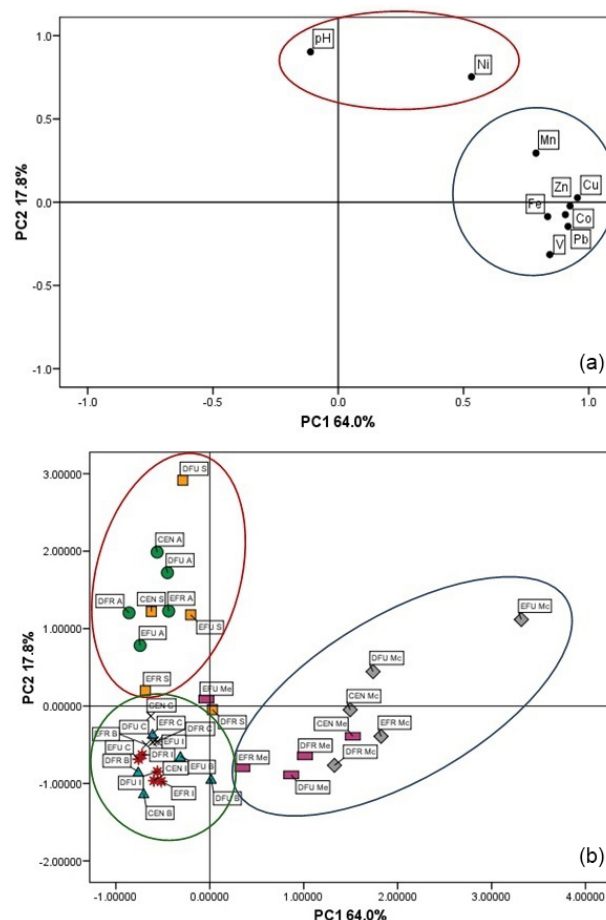elements compared to the other samples and belong to the same cultivation farm.

Figure 2. (a) Loadings graph for the two first principal components. (b) Scores graph for PC2 × PC1 for soil samples collected on farms from grape cultivation Italy Moscato, "*Itália Melhorada*" , Arra-15, Scarlotta, Crimson, Benitaka and BRS Isis in the city of Petrolina, Pernambuco. Italy Moscato soil (◆), "*Itália Melhorada*" soil (▬), Arra-15 soil (●) Scarlotta soil (■), Crimson soil (✕), Benitaka soil (▲) and BRS Isis soil (★).

Along the positive values of the PC2 axis, the variables related to the Ni concentration and pH values governed the second group formed by the soil samples from the Arra-15 and Scarlotta grapes. This behavior was due to high values found for Ni concentration and moderately basic pH values in these samples, since the presence of Ni in the soil is inversely related to pH.[25]

It can be noted that the third group formed by cultivation soil samples of the Crimson, Benitaka and BRS Isis varieties was agglomerated among the samples for presenting the lowest concentrations of Co, Mn, Ni, Pb and Zn in the negative scores of PC1 and PC2. These samples belong to the same cultivation farm, so these results may be associated with the chemical composition of the soil in that area.

Average accumulation rate of elements in grape

Essential elements such as Cu, Fe, Mn and Zn may be associated with various soil components, such as organic matter, clay, oxides, silicates and carbonates, which influence the soil's ability to retain or mobilize these elements.[21]

Thus, the accumulation ratio (AR) was used to analyze the ability of elements accumulation in grapes. In addition, it can provide data for comparing accumulation ratios between different grape varieties and soil types. The AR is determined by the ratio of the concentration of Cu, Fe, Mn and Zn in plant parts (grape) in relation to the pseudo-total concentration level in the topsoil ($AR = C_{must\ of\ grape}/C_{soil}$).[14] Accumulation rates are shown in Table 6 for all grape varieties and respective soils.

Table 6. Accumulation ratio of average values of concentrations of grape must and soil samples collected in Pernambuco state, Northeast, Brazil

Grape variety	Cu	Fe	Mn	Zn
Italy Moscato	0.03	0.0001	0.001	0.003
"*Itália Melhorada*"	0.01	0.0001	0.001	0.002
Arra-15	0.01	0.0003	n.d.	0.005
Scarlotta	0.04	0.0001	0.001	0.005
Crimson	0.02	0.0009	n.d.	0.02
Benitaka	0.01	0.0006	n.d.	0.02
BRS Isis	n.d.	0.0006	n.d.	0.01

n.d.: not determined.

Vystavna *et al.*[14] found higher accumulation ratios in Chardonnay grapes and soils from southeastern Crimea in Ukraine, the descending order was Zn (0.61) > Cu (0.29) > Pb (0.03). However, they showed that Cu is more readily accumulated than Zn and other elements, similar to the order of decreasing average accumulation ratios that was found (Cu > Zn ≥ Mn ≥ Fe) for most grape varieties and soil in the proposed work.

Only the Benitaka grape samples showed AR values for Zn higher than for Cu, and Fe in the Arra-15, Crimson, Benitaka and BRS Isis grape samples that showed AR higher than Mn. This can be explained by specific strategy of absorption/evasion of the vines aiming at the satisfaction of nutrition, prevention of toxicity, difference in the partition coefficient (ionic charge/ionic radius ratio) of the elements that induces the difference in mobility and retention, difference in the soil type and grape variety, among others.[21]

Moreover, the values in Table 6 show that Cu is more easily accumulated in Scarllota grape samples. Mn is more easily accumulated in samples of Italy Moscato and "*Itália Melhorada*" grapes. Fe and Zn are more easily accumulated in samples of Crimison, Benitaka

and BRS Isis grapes that are varieties belonging to the same cultivation farm. The results obtained with the AR complement those obtained with the PCA, providing a separation between the profiles of the must varieties, in addition, it increases the capacity of the vine to transport elements from the soil to the grape.

Conclusions

The results of the concentrations of essential elements (Ca, Cu, Fe, K, Mg, Mn, Se and Zn) and potentially toxic (As, Al and Se) allowed to identify trends or characteristics of different types of grape must, in order to draw a preliminary profile for each grape variety.

The PCA analysis clearly showed a good separation of samples in terms of mineral constituents. It was possible to perceive the highest concentrations of As, Mg and Se in the grape must cultivars Arra-15 and Scarlotta. Most of the points collected from the samples of grape must with Italy Moscato seed were characterized by high concentrations of Cu and Mn. K concentration defined the seedless wort samples of "*Itália Melhorada*" grapes and the Crimson and Benitaka grape must varieties presented higher concentrations of Al, Fe and Zn.

Although some soil samples showed concentrations of Co, Cu and Ni higher than the prevention values (VP), no sample exceeded the value stipulated for an intervention in agricultural soils based on Resolution No. 420/2009 of the CONAMA. The proposal to establish a regional geochemical base for the vine cultivation areas in the city of Petrolina, Pernambuco, Northeast, Brazilian was appropriate, since it probably leads to lesser misunderstandings when compared to works that use the global geochemical base. In addition, calculated values of EF and I_{geo} contributed to the classification in relation to the level of contamination of the area, presenting similar results in relation to the concentrations of Ni and Cu that are probably undergoing anthropic enrichment. Accumulation rate results can provide data to compare accumulation rates between different grape varieties and soil types.

Moreover, this work has an important contribution since it resulted in unprecedented information for different grape must varieties, which added up to the mineral food composition tables. In addition, the results may provide markers and indicators of geographic location of the varieties, which can serve to increase the production and quality of grapes produced for the consumer market.

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Author Contributions

Vanessa S. Santos was responsible for the conceptualization, methodology, validation, formal analysis, investigation, data curation, writing original draft, visualization; Rennan G. O. Araujo for data curation, writing review and editing, visualization; Tarcísio Silva Almeida for methodology, validation, data curation, writing review and editing, visualization; Wagna Piler C. dos Santos for data curation, writing review and editing, visualization; Maria das Graças A. Korn for resources, data curation, writing review and editing, supervision, project administration, funding acquisition.

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