foods

MDPI

Article

From soil to grape and wine: the geographical variation of elemental profile in China

Xiaoyun Hao[1], Feifei Gao[1], Hao Wu[5], Yangbo Song[1], Liang Zhang[1], Hua Wang[1,2,3,4]*,Hua Li[1,2,3,4]*

[1] College of Enology, Northwest A&F University, Yangling, Shaanxi 712100, China; haoxiaoyun@nwafu.edu.cn (X.H.); gaofeifei@nwafu.edu.cn (F.G.); ys792@cornell.edu (Y.S.); zhangliang20@nwafu.edu.cn (L.Z.)
[2] Shaanxi Engineering Research Center for Viti-viniculture, Yangling, Shaanxi 712100, China
[3] China Wine Industry Technology Institute, Yinchuan, Ningxia750021, China
[4] Engineering Research Center for Viti-Viniculture, National Forestry and Grassland Administration, Yangling, Shaanxi712100, China
[5] Food Inspection and Quarantine Center, Shenzhen Customs, Shenzhen 518000, China; whakyo@foxmail.com (H. W.)
* Correspondence: wanghua@nwafu.edu.cn (H.W.); lihuawine@nwafu.edu.cn (H. L.); Fax: +86-8709-1099 (H.W.)

Abstract: Elemental profiles are frequently applied to identify the geographical origin and the authenticity of food products to quality guarantee. The concentrations of fifteen major and trace elements (Na, Mg, K, Ca, Al, Fe, Mn, Cu, Zn, Rb, Sr, Li, Cd, Cs, and Ba) were determined in the soils, grape berries, and wines from six regions in China by inductively coupled plasma mass spectrometry (ICP-MS). The purpose was to reveal the geographical variation of elements in system soil-grape-wine, and to obtain the crucial elements for origin recognition. Distinct composition of elemental concentrations occurred in soils, grape berries, and wines among the six studied regions by ANOVA analysis. All the heavy metals were under the maximum limit admitted. The bioconcentration factor of system soil-grape and transfer factor of system wine-grape were calculated. No heavy metals enrichment was found in grape berries. Moreover, this study explored the relationships of elements between the pairs of soil-grape, grape-wine, and BCF-environmental factor by Pearson's correlation. The elements K, Sr, and Li showed apparent correlations related to the origin. To verify the traceability of these three elements, linear discriminant was introduced. It was confirmed that the elements K, Sr, and Li were strongly linked to the provenance. These elements presented their potential for origin identification in China.

Keywords: Geographical variation, Elemental profile, Environmental factor, ICP-MS, Chinese regions

Citation: Lastname, F.; Lastname, F.; Lastname, F. Title. *Foods* **2021**, *10*, x. https://doi.org/10.3390/xxxxx

Academic Editor: Firstname Lastname

Received: date
Accepted: date
Published: date

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Copyright: © 2021 by the authors. Submitted for possible open access publication under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/licenses/by/4.0/).

1. Introduction

The geographical origin of food products provides an extra guarantee for the quality, authenticity, and type [1]. As a natural product, the origin of wine is an essential basis for the quality characteristics of wine products, which determines the style of wine and plays a decisive role in the choice of consumers [2]. Hence, establishing the geographical origin of wines became a major concern for many countries worldwide [3].

After a long period of significant expansion, the global vineyard areas and grape production increased slowly, the wine consumption even showed 3% decrease compared to 2019 due to Covid-19 crisis. Concerning China, the growth of the vineyard (758 kha) in 2020 is slowly growing by 0.6% compared to 2019. The consumption of wine (12.4mhl) in 2020 showing a 17.4% drop with respect to 2019. However, China is still in the third position in the vineyard areas in the world in 2019 and 2020, and also the sixth highest consuming country [4]. Further, with the sharp decline in imported wine, the demand for domestic wine will increase, and the origin will become a viable value-added processing

option. As the wine industry expands into new provinces such as Shaanxi, Shanxi, and Inner Mongolia, so does the demand for geographical origin identification in China.

At present, the main techniques have been implemented for wine origin identification including spectrum (near-infrared, middle-infrared, and nuclear magnetic resonance) [5-7], chromatography (gas chromatograph and liquid chromatography) [8-10], and mass spectrometry [11,12]. Mass Spectrometry (MS), such as Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and Isotope Ratio Mass Spectrometry (IRMS), has become a front-line technology rapidly replacing other methods in many fields of food science. Especially in the field of food authentication, due to unsurpassed advantages such as high sensitivity, selectivity, throughput and multi-analyte capabilities of MS techniques [13-16]. Therefore, numerous studies have been dedicated to the application of mineral elements and isotopes analysis in the provenance of wine [12, 17-19]. Unlike the analysis of isotopes, mineral elements analysis is fast, inexpensive, and extensive. As a complex matrix, wine is rich in elements (major, trace, and rare earth elements) [20]. The elements of primary origin in wine are mainly from the grapes by absorbing from the soils on which vines are grown. Besides, anthropogenic factors such as the viticulture practices and vinification processes can also contribute to the elemental profiles [20]. Among the factors mentioned above, the geochemistry of vineyard soil plays a fundamental role in the elemental uptake of grapevine [16].

Consequently, several different countries have successfully identified geographical origins by elemental analysis, such as Italy [18], Greece [21], Japan [22], United States [23], South Africa [24], Australia [25], Romania [26], and Slovenia [27]. What's more, these studies cited the superiority of the ICP-MS technique to determine the elements. Simultaneously, multivariate statistical analyses such as principal component (PCA), linear discriminant (LDA), and cluster analysis (CA) have been widely employed in the classification and patterns modeling of wine regions. Generally, most of the studies for wine origin identification were conducted based on the analysis of elemental concentrations in wine combined with chemometric methods. Conversely, fewer of them evaluated the elemental migration and bioaccumulation in the soil-grape-wine system. Furthermore, particularly for Chinese wine regions, there are little detailed published data on the elemental profiles in soils, grape berries, and wines [28, 29, 30]. To our knowledge, there is no studies combing the bioconcentration factors (BCF), transfer factors (TF), and environmental conditions (precipitation, temperature, average relative humidity, latitude, and altitude) with elemental profiles in order to obtain the characteristic elements for an accurate wine classification in China.

In our study, "Meili" (*Vitis vinifera* L.), an innovative cultivar with strong disease-resistance, bred by the Enology College, Northwest A&F University From 1982 to 1999, was chosen as the research object [31]. This cultivar was selected to resist the disease (*Plasmopara viticola* and *Sphaceloma ampelinum*) and cold weather [31]. After years of cultivation experiments in Shaanxi, Shanxi, Inner Mongolia, and other areas, this variety shows strong disease-resistance, stable quality and is a medium variety for producing distinct and flavor red wine [32, 33, 34]. Recently studies revealed that the uptake of major and trace elements could be affected by rootstock types [18, 35, 36]. Although Pisciotta et al. [37] observed that the different grafting combinations were not able to induce significant differences in the rare earth elements of Y, La, and Lanthanoids, their abundance in soils is scatter and need to be normalized. Our study object, the cultivar of "Meili" (*Vitis vinifera* L.) is own-rooted with a purity line named "8804", which could avoid the interferences of rootstocks on the major and trace elemental concentrations [31].

Therefore, comparisons among elements in soils, grape berries, and wines from six regions were performed to explore the possible distinct composition in different regions. The relationships between the two pairs of soil-grape and grape-wine were considered to obtain geographical variations of the mineral elements. Meanwhile, to reveal the migration of the elements in system soil-grape-wine, the BCF of system soil-grape and TF of system wine-grape were calculated. Further, the relationships between BCF and

environmental factors (temperature, precipitation, average relative humidity, altitude, and latitude) were investigated to obtain the elemental profiles that close relative to the geographical origins. Linear discriminant was employed to confirm the geochemical markers of Chinese wine.

2. Materials and Methods

2.1. Sample collection

Soil, grape, and wine samples were collected from three Provinces (Shaanxi, Shanxi and Henan) and Inner Mongolia Autonomous. These provinces are the distinctive viticultural regions in China. Samples (soil, grape, and wine) were collected from six wine regions in 2018 harvest year: YL (Yangling, Shaanxi), BLY (Bailuyuan, Shaanxi), HY (Heyang, Shaanxi), XX (Xiaxian, Shanxi), MQ (Minquan, Henan), and WH (Wuhai, Inner Mongolia Autonomous) regions (Figure 1). Table 1 shows the information of all samples, including geographical and climatic factors during the veraison (July) and mature periods (August).

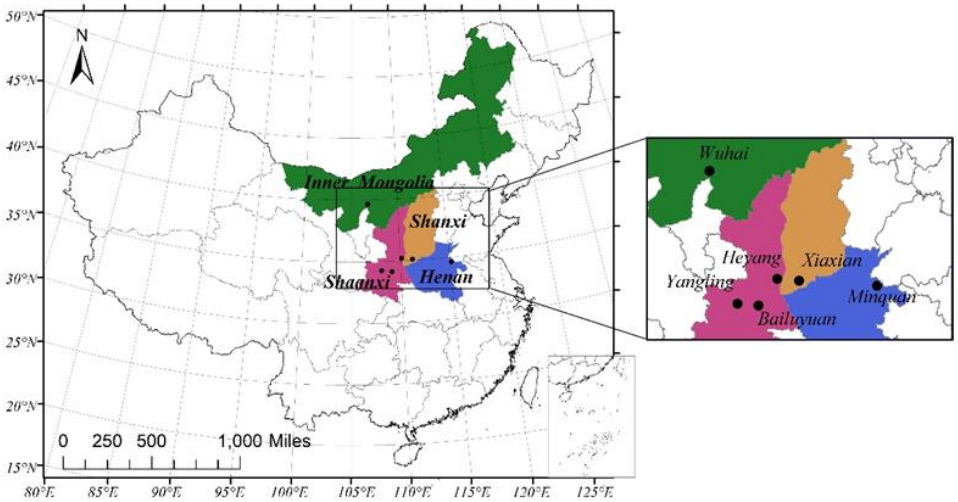

Figure 1. Map of six regions where soil, grape berries, and wine samples were collected: YL (Yangling, Shaanxi), BLY (Bailuyuan, Shaanxi), HY (Heyang, Shaanxi), XX (Xiaxian, Shanxi), MQ (Minquan, Henan), and WH (Wuhai, Inner Mongolia Autonomous).

The study is focused on wines made through micro-vinification of "Meili" monocultivar. One hundred grape berries were picked from 20 bunches at random for each sampling plot and five grape samples for each region. Also, 25 kg of grape samples were collected from each region for winemaking. The plastic containers used for storing and treating the samples were cleaned to avoid contamination. The grape berries were stored at -20 ℃ until analysis. Furthermore, the 25 kg of grape samples for winemaking were destemmed and crushed into the glass fermenters immediately after taken back to the laboratory.

Soil samples (n=30) were collected from the corresponding vineyards. To reduce the effect of any surface contamination (pollution and fertilizer), five soil samples (1.5 kg each) were collected from a depth of 10 to 60 cm, about 30 cm around each grapevine in the vineyard. In the laboratory, soil samples were dried to a constant weight and sieved through a 2 mm mesh. Homogenization was performed by quartering and pulverization procedures.

Table 1. Information on samples, locations and weather conditions in July and August of the six studied regions in China.

Regions	Latitude	Longitude	Altitude (m)	Precipitation (mm)	Average temperature (℃)	Average relative humidity (%)
Yangling, Shaanxi (YL)	34.3	108.1	521	262.7	27.2	74.9
Bailuyuan, Shaanxi (BLY)	34.2	109.1	713	185.8	28.8	66.1
Heyang, Shaanxi (HY)	35.2	110.2	716	158	27	71
Xia county, Shanxi (XX)	35.1	111.2	402.9	66.6	29	58.2
Minquan, Henan (MQ)	34.7	115.2	60.6	538.8	28.1	82.3
Wuhai, Inner Mongolia (WH)	39.7	106.8	1105.6	171.1	23.3	59.4

Note: Information obtained from National Meteorological Information Center of China.

2.2. Sample pretreatment

Before elemental analysis, the samples were carefully prepared to avoid chemical and physical interactions. All the tests were carried out at the Food Inspection and Quarantine Center of Shenzhen Customs in China.

2.2.1. Fermentation process

Detailed micro-vinification procedures were performed as followed: grape clusters were destemmed and crushed into 5 L glass fermenters at the laboratory of Enology College, Northwest A&F University. After a three-day cold maceration at a temperature less than 10 ℃, the must was warmed to 21 ℃ for natural fermentation using wild *Saccharomyces cerevisiae* from the grape skin itself. After two days of fermentation at 21 ℃, the fermentation temperature was allowed to increase to 28 ℃ until the alcoholic fermentation was complete. No malolactic fermentation was performed. Then, molecular SO_2 was adjusted to 0.6 mg/L with potassium metabisulfite (Food Grade, China).

2.2.2. Digestion process

2.2.2.1. Grape berries

Grape berries were rinsed with Milli-Q water (resistivity 18.2 MΩ/cm, Milli-Q Advantage A10, USA) and blotted with clean paper. 100 berries were homogenized using a homogenizer (JYL-C010 Jiuyang, China), and acid digested using a microwave system (Ethos One, Milestone, American) with 75 mL Teflon digestion vessels. 1g homogenized samples were weighed inside, and 5ml concentrated nitric acid (GR, Merck, Germany) was added. Teflon digestion vessels were pre-cleaned in 10% nitric acid solution (GR, Merck, Germany) to avoid cross-contamination. Then, the vessels were transferred into the microwave digestion instrument for digestion by application of the program described from Geana. et al. [26]. After cooling to ambient temperature, the content was quantitatively transferred into a 50 ml volumetric flask and brought to the volume with Milli-Q water. A blank calibration sample was made of HNO_3, water and a quality control sample were also prepared using the above procedure.

2.2.2.2. Wine

The wine digestion was carried out in the Teflon digestion vessel adding 2 ml of wine and 5 ml of HNO_3. The vessels already capped were placed in the microwave oven, followed by applying the program described from Geana et al. [26]. The cooled digests were transferred into a 50 mL volumetric flask. The digestion tubes were rinsed three times

with Milli-Q water, and this water was transferred into the volumetric flask and diluted with milli-Q water up to 50 mL.

2.2.2.3. Soil

Soil samples were dried at 105 ℃ for 24 h, then homogenized and passed through a 20 mesh sieve to obtain very fine particles. An amount of 0.25 g of powder was weighted in a 50 mL Teflon digestion vessel, adding 3 mL of 65% HNO_3, 2 mL concentrated HCl (GR, Merck, Germany), and 1 mL concentrated HF (GR, Merck, Germany). The digestion was carried out with the program also from Geana et al. [26]. The final digests were transferred to volumetric flasks and made up to 50 mL with Milli-Q water.

2.3. Elemental analysis

The elemental determination was performed with an inductively coupled plasma mass spectrometer (ICP-MS) (ICAP-Q, Thermo Fisher, USA) equipped with an ASX-260 auto-sampler (CETAC Thermo fisher, USA), a Burgener nebulizer (1.0 mL/min), nickel cones, and a peristaltic sample delivery pump. The operating conditions were described by Rodrigues et al. [38].

The quantified concentrations of elements were performed using an external standard of a calibration mixture standard solution (CLMS-2, SPEX CertiPrep, USA) in 0.5% nitric acid. The calibration range for major and trace elements was from 0.1 to 10 mg/L and from 0.001 to 1 mg/L, respectively. Rh and In (50μg/L) were included as an internal standard to control instrumental drift correction. The recovery rate should be maintained at 90%~110%.

2.4. Statistical analysis

The bioconcentration factor (BCF) was used to assess the transfer of elements from soils to grape berries were calculated using the equation below:

$$BCF = C_g / C_s \quad (1)$$

Where C_g and C_s are the concentrations of the elements in grape berries and soils, respectively.

The transfer factors (TF) were calculated to assess traceability and bioavailability of the elements from grape berries to wines.

$$TF = C_w / C_g \quad (2)$$

The C_w and C_g represent the concentrations of the elements in wines and grape berries, respectively.

One-way analysis of variance (ANOVA) and Duncan's test were applied to investigate whether the differences in the elemental concentrations in soil, grape berries, wine samples, BCF, and TF relative to six studied origins. Differences among the regions were considered significant when $p < 0.05$. Pearson correlation analysis was carried out to confirm the relationship between the two pairs of soil-grape and grape-wine for the elemental concentrations. Furthermore, the relationships between environmental factors (temperature, precipitation, average relative humidity, altitude, and latitude) and BCF values were analyzed to obtain some influences on the element uptake of the grape berries from the soils. Linear discriminant analysis (LDA) was utilized to evaluate whether the samples could be classified amongst geographical origins according to F-value. The robustness of the classification model was evaluated using a cross-validation test based on the "leave-one-out" procedure. All procedures were performed using SPSS 20.0 software (IBM Inc., USA).

3. Results

3.1. Elemental compositions

3.1.1. Elemental concentrations in soils

The mean elemental concentrations and standard deviations for soil samples collected from six regions are summarized in Table 2. Regarding the differences in the six studied regions, the determined fifteen elements all showed significant differences ($p < 0.05$), demonstrating that soils from different regions have a characteristic elemental

profile. Among the major elements, Fe was the most concentrated, followed by K, Ca, Al, Na, and Mg. Fe presented the highest values in YL and BLY soils, followed by XX and HY; the lowest values were found in MQ and WH. With regard to the trace elements, the concentrations order was, Mn> Sr> Zn> Rb> Li> Cu> Ba> Cs> Cd, except an outlier of Ba (mean value 334.37 mg/kg) in BLY. The concentration of Mn displayed the highest value in BLY, followed by YL, XX and HY, the lowest values were found in WH and MQ regions. In general, most of the elements presented the highest values in YL, BLY, and XX, intermediate higher values found in HY, the lowest values in WH and MQ regions.

Table 2. Means and standard deviations of measured elements corresponding to soils according to geographical origins.

element	YL	BLY	HY	XX	MQ	WH
Na	5317.55±226.46d	6624.58±758.57b	6441.88±194.29bc	5893.36±346.36c	9228.12±495.13a	6684.22±312.53b
Mg	4701.24±511.01b	5838.5±1362.85a	2985.63±370.36c	5079.65±562.74ab	3229.44±394.72c	3411.39±447.14c
K	28280.61±1363.73a	21202.23±2563.57b	15444.1±2176.28c	27402.92±2441.51a	25504.47±3140.61a	22187.01±907.26b
Ca	22135.92±1170.75a	16496.1±2742.05b	22983.59±3520.55a	25826.24±5193.44a	22961.91±2773.03a	22500.14±3786.26a
Al	11551.09±6153.12c	18523.64±3026.34ab	5437.57±1872.83d	20263.73±3627.75a	14823.38±1480.85bc	13659.4±1425.99c
Fe	32613.70±987.11a	35871.31±5642.21a	17183.05±2053.38c	24728.49±3330.3b	8843.31±2321.8d	9343.85±1613.26d
Mn	699.97±28.71b	802.08±143.57a	534.77±18.05c	559.76±16.92c	358.76±37.94d	325.56±20.11d
Cu	29.28±1.25a	31.42±0.93a	25.16±1.36b	24.91±2.49b	13.14±2.49c	12.44±1.19c
Zn	80.24±3.00a	62.53±0.86c	73.15±2.36b	72.49±5.73b	48.15±3.23d	45.88±3.16d
Rb	31.60±17.3b	6.35±1.42c	10.36±3.56c	64.58±33.14a	56.87±3.44a	56.86±5.9a
Sr	182.48±11.45b	73.08±1.36d	154.93±3.17c	207.36±17.58a	215.87±19.98a	162.47±7.54c
Li	24.44±0.97c	45.05±1.69a	34.53±3.34b	25.95±1.02c	15.27±1.16d	14.6±1.53d
Cd	0.34±0.02a	0.20±0.02d	0.26±0.01c	0.28±0.01b	0.17±0.01e	0.17±0.02e
Cs	6.64±0.44a	1.19±0.30d	3.99±0.66b	7.21±1.75a	2.85±0.35c	3.10±0.37bc
Ba	6.10±1.06b	334.37±11.92a	8.66±1.33b	9.23±4.79b	8.23±0.55b	7.05±0.9b

Note: The elemental concentrations of the soil samples are expressed in mg/kg; YL= Yangling; BLY= Bailuyuan; HY= Heyang; XX= Xiaxian; MQ= Mingquan; WH= Wuhai; Different letters in the same row indicate statistically significantly different ($P < 0.05$).

3.1.2. Elemental concentrations in grape berries

Table 3 displays the mean elemental concentrations and standard deviations of grape berries. Ten elements (Na, Mg, K, Mn, Rb, Sr, Li, Cd, Cs, and Ba) showed significant differences among the six regions ($p< 0.05$). The concentration order of major elements was K> Mg> Na. K showed the highest values in XX region, with intermediate values in YL, BLY, MQ, and WH regions, the lowest values were found in HY region. Concerning the trace elements, the concentration decreased in the order Rb> Sr> Mn> Ba> Li> Cs> Cd. The concentration ranges of Rb and Sr were varied greatly among the six regions; their mean values were from 0.99 mg/kg (WH) to 7.34 mg/kg (BLY) and from 0.41 mg/kg in BLY to

6.98 mg/kg in XX, respectively. Overall, most elements in XX presented the highest values, the lowest values were found in WH region.

Table 3. Means and standard deviations of measured elements corresponding to grape berries according to geographical origins.

element	YL	BLY	HY	XX	MQ	WH
Na	3.29±0.29c	3.19±0.47c	3.83±0.50c	7.77±2.04b	12.64±1.38a	3.63±0.33c
Mg	120.85±40.62b	106.40±16.17b	110.67±25.12b	175.06±17.80a	120.77±28.30b	127.31±21.65b
K	2692.41±165.80 b	2739.84±118.36 b	1929.11±134.27 c	3045.90±233.00 a	2542.65±233.15 b	2506.37±175.88 b
Ca	235.86±92.61a	151.70±42.11a	242.07±82.97a	222.20±53.22a	225.28±84.79a	231.18±61.82a
Al	1.25±0.12ab	1.07±0.18b	1.65±0.63a	1.60±0.26a	1.47±0.06ab	1.33±0.47ab
Fe	6.87±1.78a	6.34±4.54a	6.68±1.43a	6.34±0.62a	6.18±0.96a	5.24±0.90a
Mn	1.84±0.43b	0.85±0.18c	1.65±0.46b	2.65±0.40a	0.79±0.15c	0.86±0.22c
Cu	2.56±0.22ab	1.89±0.30b	3.33±3.23ab	4.48±2.7a	2.52±0.77ab	1.72±0.26b
Zn	1.27±0.21b	1.47±0.52ab	1.52±0.39ab	1.81±0.43a	1.36±0.20ab	1.20±0.28b
Rb	6.00±0.88b	7.34±0.37a	4.32±0.37c	4.19±0.71c	3.85±1.49c	0.99±0.35d
Sr	1.46±0.26c	0.41±0.04d	1.15±0.25cd	6.98±1.41a	1.67±0.67c	3.05±0.71b
Li	6.48±0.76c	3.64±0.44d	6.83±0.47c	12.37±2.27b	11.26±1.89b	23.06±2.14a
Cd	1.70±0.35a	0.86±0.10b	0.70±0.28b	0.32±0.08c	0.37±0.06c	0.22±0.05c
Cs	10.09±1.12b	11.91±0.51b	18.60±0.97a	9.60±2.80b	10.75±5.75b	2.53±1.30c
Ba	300.73±118.92a b	114.00±22.05c	178.86±31.27bc	381.6±106.75a	382.76±178.40a	259.34±22.66ab

Note: The elemental concentrations of the grape berries are expressed in mg/kg from Na to Sr and in μg/kg from Li to Ba, respectively; YL= Yangling; BLY= Bailuyuan; HY= Heyang; XX= Xiaxian; MQ= Mingquan; WH= Wuhai; Different letters in the same row indicate statistically significantly different ($P < 0.05$).

3.1.3. Elemental concentrations in wines

The comparison of elemental concentrations performed by grouping the wines from six regions are summarized in Table 4. It revealed significant differences for all the fifteen elements among the six regions ($P< 0.05$). As observed, K was the most concentrated element among the major elements, followed by Mg and Ca, while Na was found with the lowest concentration. With regard to the trace elements, the contents in the studied wines decreased in the order Rb> Fe> Zn> Sr> Mn> Al> Cu> Ba> Li> Cs> Cd. The concentrations of Mn, Cu, Zn, Rb, Sr, Li, Cs, and Ba presented distinctive values among the six studied areas ($P<0.05$). The wine samples from XX showed the highest concentrations of Mn, Zn, and Sr. Besides, the lowest values of elements (Fe, Zn, Sr, Li, and Ba) were found in BLY region, the concentrations of Mn, Rb, Cd, and Cs displayed the lowest values in WH. Moreover, the orders of the major and trace elements' concentrations in wine were the same to the grape berries.

Table 4. Means and standard deviations of measured elements corresponding to wines according to geographical origins.

element	YL	BLY	HY	XX	MQ	WH
Na	6.19±0.03e	6.88±0.08d	5.78±0.01f	17.79±0.19b	19.69±0.14a	7.37±0.09c
Mg	179.38±1.90c	152.37±0.94f	170.39±0.83e	248.09±2.15a	197.76±0.89b	174.82±0.53d

K	3120.46±16.18b	2683.96±28.20d	1855.56±3.03f	4044.25±5.30a	2998.18±21.02c	2134.68±2.43e
Ca	120.19±1.01a	92.07±1.66c	116.26±15.69ab	72.49±1.40d	109.06±0.42b	87.57±0.22c
Al	0.36±0.01b	0.38±0.09b	0.45±0.05b	0.73±0.27a	0.48±0.01b	0.52±0.22b
Fe	1.95±0.01b	1.10±0.25d	1.95±0.02b	2.19±0.17a	1.61±0.01c	1.64±0.02c
Mn	0.95±0.05b	0.57±0.01e	0.92±0.01c	1.42±0.01a	0.61±0.01d	0.52±0.01f
Cu	0.22±0.00e	0.35±0.01a	0.27±0.01c	0.32±0.01b	0.21±0.00f	0.24±0.01d
Zn	1.43±0.01c	0.71±0.01f	1.50±0.01b	2.06±0.07a	1.28±0.01d	0.98±0.01e
Rb	4.88±0.04a	4.68±0.07b	2.58±0.02d	3.36±0.02c	2.36±0.03e	0.69±0.02f
Sr	0.63±0.01d	0.29±0.01f	0.55±0.00e	1.94±0.02a	0.84±0.01c	1.22±0.01b
Li	7.20±0.11d	2.67±0.06f	6.49±0.06e	18.91±0.11b	17.32±0.20c	24.74±0.31a
Cd	0.36±0.05c	0.56±0.03a	0.45±0.03b	0.56±0.03d	0.22±0.02d	0.14±0.03e
Cs	12.29±0.50b	10.62±0.06c	16.98±0.07a	7.84±0.07e	8.27±0.04d	2.29±0.04f
Ba	120.14±0.59b	69.51±1.04f	84.59±0.41e	109.42±0.23d	145.51±1.00a	111.83±0.89c

Note: The elemental concentrations of the wine samples are expressed in mg/L from Na to Sr and in μg/L from Li to Ba, respectively; YL= Yangling; BLY= Bailuyuan; HY= Heyang; XX= Xiaxian; MQ= Mingquan; WH= Wuhai; Different letters in the same row indicate statistically significantly different (P < 0.05).

3.2. Relationships of elemental concentrations between two pairs, soil-grape and grape-wine

3.2.1. Correlation of elemental concentrations between soil and grape berries

In order to identify the correlation of elemental concentrations between soil-grape and grape-wine, Pearson correlation analysis and the linear curve fitting were performed. According to the correlation coefficients and linear curve fitting, three elements show significant correlations between soil and grape berries (Figure 2). Two of the elements (K, Cd) present positive correlations (both of their r=0.66, P<0.01) (Figure 2 a and b), while Li shows negative correlations (r=-0.74, P<0.01) between soil and grape berries (Figure 2 c).

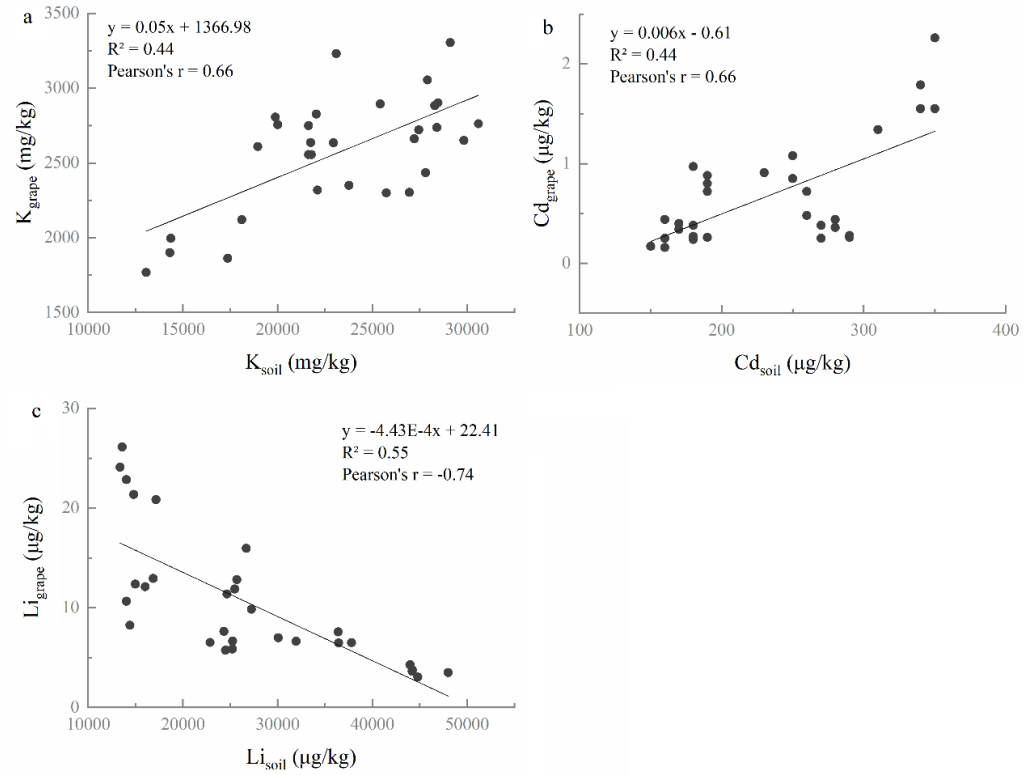

Figure 2. The relationships for the elements between soils and grape berries.

3.2.2. Correlation of elemental concentrations between grape berries and wine

Figure 3 presents good positive relationships between grape berries and wine. Of the 15 elements, six elements (K, Mn, Rb, Sr, Li, and Cs) show a positive correlation between grape berries and wine (P<0.01).

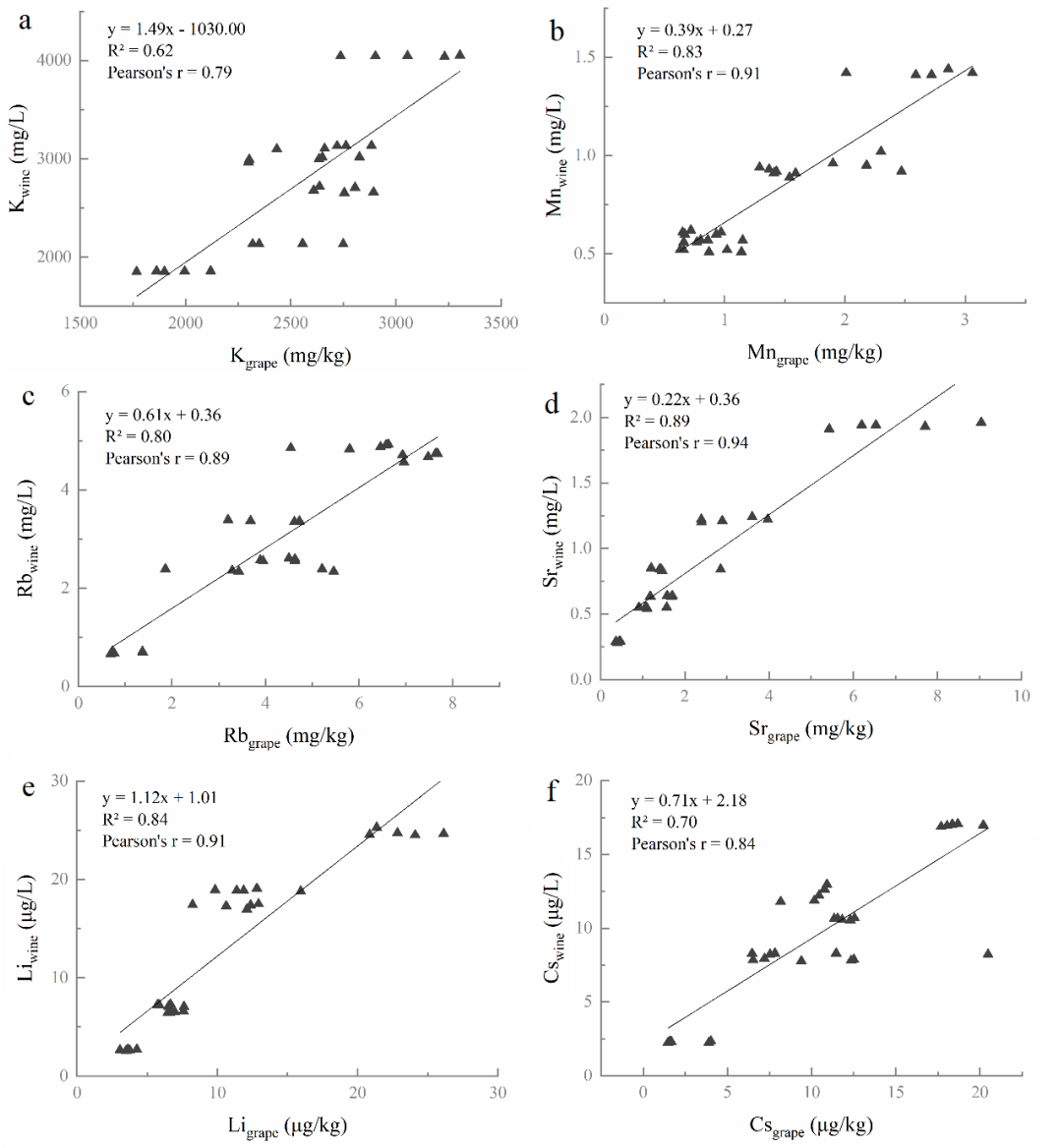

Figure 3. The relationships for the elements between grape berries and wines.

3.3. Bioconcentration factor and transfer factor

3.3.1. Bioconcentration factor in different regions

According to the one-way ANOVA and Duncan's test, the concentrations of all the fifteen elements in the soil were significantly different (P<0.05), and ten of the elements in grape samples showed significant differences (P<0.05). As shown in Suppl. Table 1, the ability of grape berries to absorb different elements varied greatly. After assessing the elemental bioconcentration, the values of the BCF for most of the investigated elements were lower than 1. The exception was Rb with a BCF higher than 1(BCF> 1) in BLY region.

3.3.2. Relationships among the BCF values

Pearson correlation analysis of the BCF values is shown in Suppl. Table 2. Among the fifteen BCF values, Rb and Mg showed the strongest correlation with other eleven elements correlated significantly. The BCF values of Rb showed significant positive

correlations with K (P<0.01), Cs (P<0.01), and Cd (P<0.05), while significant negative correlations with Na, Mg, Mn, Fe, Li, and Ba (P<0.01), Cu and Sr (P<0.05). The BCF values of Mg was significantly positively correlated with eight elements (Ca, Mn, Fe, Zn, Ba, Cu, Sr, and Li, the first five P<0.01, the last three P<0.05), whereas significant negative correlations were presented with Rb (P<0.01), Cd (P<0.01), and Cs (P<0.05).

3.3.3. Relationships between BCF values and environmental factors

The input and output of elements in the soil-plant system were affected by temperature, humidity, precipitation and other meteorological factors [39, 40]. As shown in Figure 4, the BCF values of Sr and Li were significantly correlated with environmental factors (P<0.01). The BCF values of Sr presented a significant negative correlation with the average relative humidity (Figure 4a, r=-0.69, P<0.01). The BCF values of Li element displayed a negative correlation (Figure 4b, r=-0.79, P<0.01) with temperature. Moreover, the BCF value of Li was positively correlated (Figure 4c, r=0.79, P<0.01) with latitude.

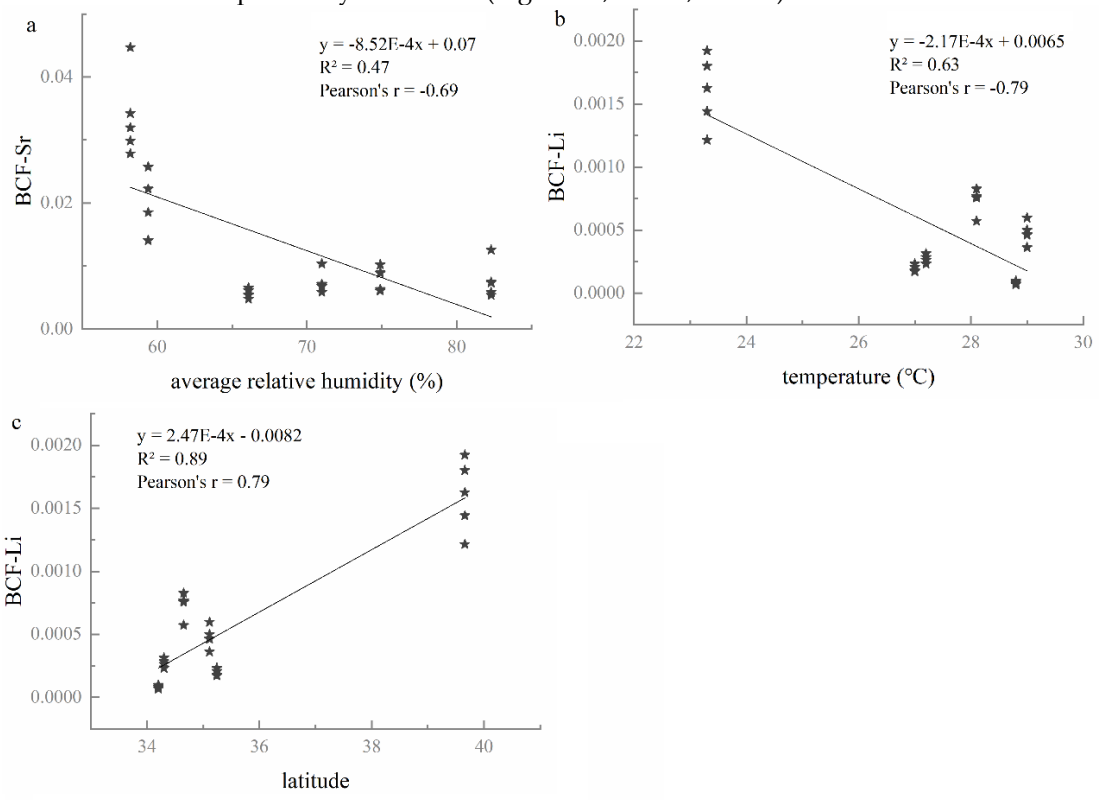

Figure 4. The relationships the BCF values and environmental factors.

3.3.4. Transfer factor in different regions

The transfer factors (TF) values of system wine-grape obtained are shown in Suppl. Table 3. The concentrations of Na and Mg in wines were higher than in grape berries from all the studied regions. Four elements (K, Zn, Li, and Cs) presented higher values in wines than in grape berries in part of regions.

3.4. Discriminant Analysis

It was concluded that K and Li had significant correlations not only between soils and grape berries, but also between grape berries and wines (Figure 2 and 3). Moreover, the BCF values of elements Sr and Li are closely related to the environment factors (Figure 4). Therefore, it was hypothesized that K, Li, and Sr were the characteristic elements that could be implemented to distinguish the six regions in this study. To approve this hypothesis, linear discriminant analysis (LDA) with a leave-one-out cross-validation test was applied to trace origin by using these three elements (K, Li, and Sr).

For soil samples, the first discriminant function (F1) plot against the second one (F2), as shown in Figure 5a. The LDA analysis allowed distinguishing among six regions with 93.3% certainty and 90% cross-validation rate, confirming the three elements (K, Li, and Sr) were useful for the geographical origin differentiation of soils in six studied areas. Li and Sr showed the highest correlation in F1 and F2, respectively, which could be the most useful tracers for the studied regions. As shown in Figure 6c, Li divided the six regions into 4 groups: BLY region, HY region, YL and XX regions, MQ and WH regions. Moreover, Sr differentiated between YL and XX, MQ and WH regions, respectively (Figure 6b).

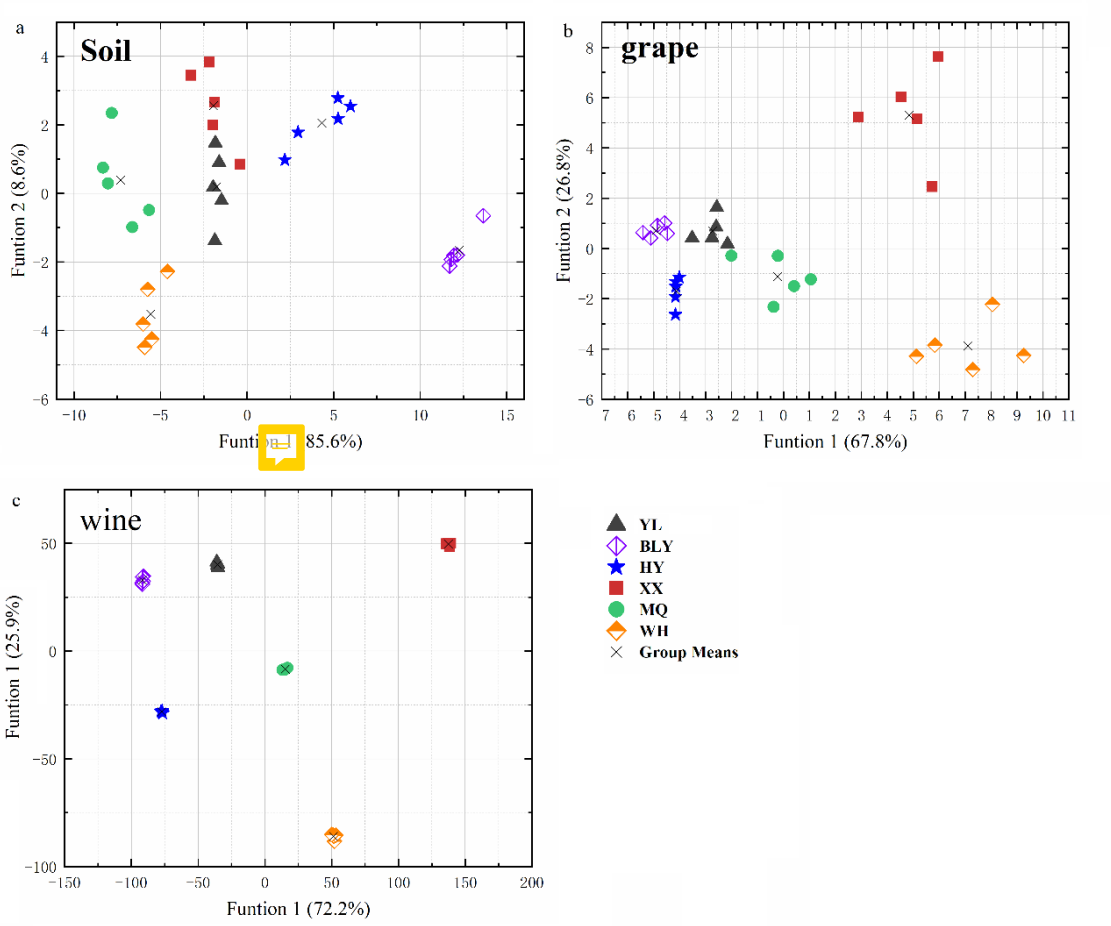

Figure 5. Linear discriminant analysis (LDA) performed on data expressed as concentrations of the three elements (K, Sr, and Li) in soil (a), grape (b), and wine samples (c) from the six studied regions.

LDA of the grape data set could classify among six studied regions with 96.7% certainty and cross-validation rate based on Sr, Li, and K (Figure 5b). Li and Sr showed the highest correlation in F1 and F2, respectively, demonstrated that they were assumed as crucial variables to distinguish amongst grape samples from the six studied regions. Li distinguished the two regions (BLY and WH) from other regions (Figure 6f), whereas Sr distinguished XX and WH from the other four regions (Figure 6e).

The LDA analysis was also applied to the wine samples with a 100% validation and cross-validation rate, indicating that Sr, Li, and K could be applied to discriminate the wine samples' geographical origin. The variables of K showed the highest correlation in F2 to the classification amongst wine from the studied regions. As shown in Figure 6g, K differentiated all the studied regions.

Our study showed an apparent regional separation of soil, grape, and wine samples, revealing that these three mineral descriptors (Sr, Li, and K) were valuable as geographical indicators.

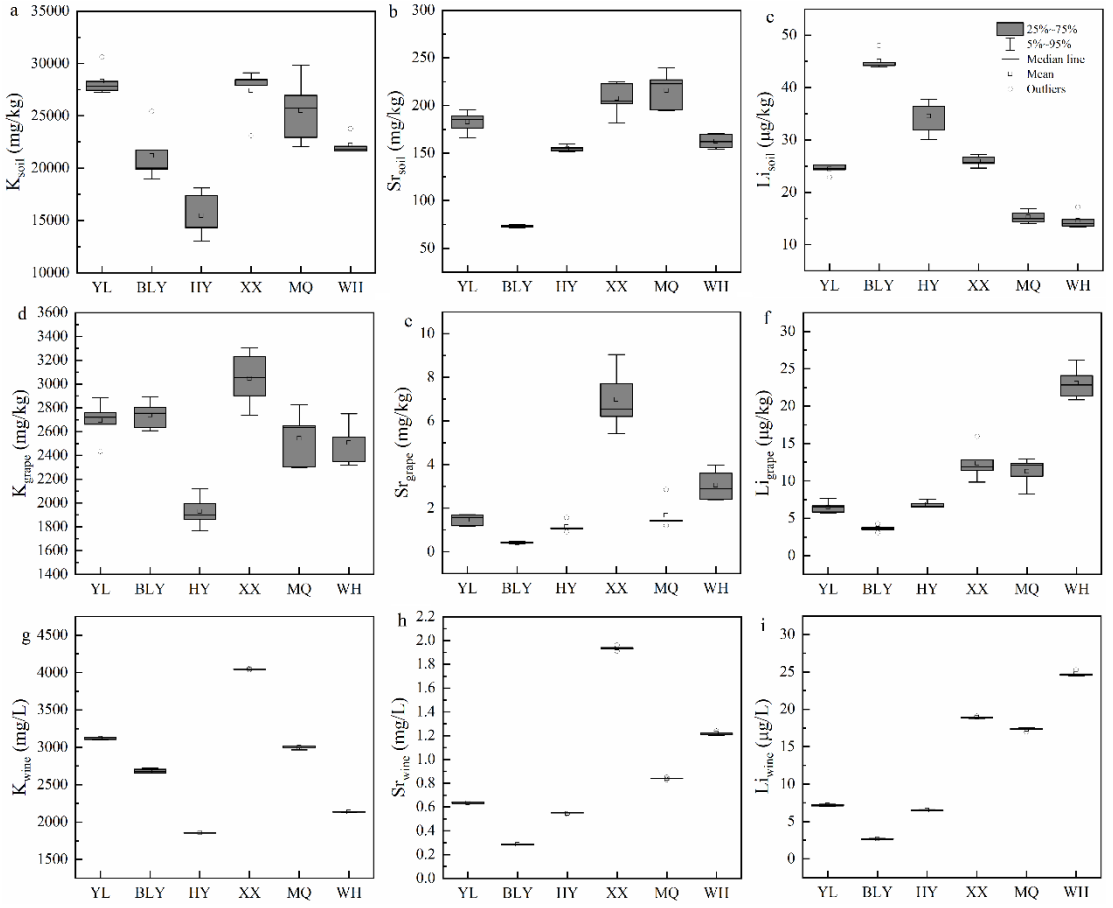

Figure 6. Box plots with elemental contents of K, Sr, and Li in soils (a, b, and c), grape berries (d, e, and f), and wines (g, h, and i) from the six regions.

4. Discussion

4.1. Geographical elemental profile in soil, grape, and wine samples

4.1.1. Geographical elemental profile in soil samples

In our study, the elemental concentrations of soil were with similar magnitude in which researchers found higher levels of these elements in the soils from Norther Italy and lower levels of from Romania [18, 26]. In addition, Zou et al. found the Sr and Ba had the highest levels among their determined elements in the soils, grapes, and wines from other seven regions in China, which is consist with our research [28]. The distinctive concentrations of elements allowed distinguishing three groups of soils (Table 2): group 1 includes the soils with high concentrations of the majority elements in YL, BLY, and XX regions; group 3 comprises soils low in most of elements in MQ and WH regions; group 2 contains soils in HY region with the intermediate concentrations which were between group 1 and 3. This association is likely in connection with the different soil types in the studied regions [41]. The soils in YL, BLY, and XX are mainly sandy loam, especially the soils of YL and BLY are composed of Eum-Orthric Anthrosols which are rich in trace elements [31, 42, 43]. Nevertheless, the soils in MQ and WH are primarily sandy soil which generally poor in trace elements [44, 45]. The soil with intermediate concentrations in HY may related to the gravel and sandy soil texture [46]. Moreover, YL, BLY, and HY belong to Guanzhong Plain in Shaanxi Province, and XX, although in Shanxi Province, is closely

to HY. Hence, the elemental composition also showed the potential to differentiate the small adjacent regions. Additionally, no soil samples in this study exceeded the maximum permissible concentration according to Chinese Soil Environmental Quality (Cu < 200 mg/kg, Zn < 300 mg/kg, and Cd < 0.6 mg/kg) (GB15618-2018) [47]。

4.1.2. Geographical elemental profile in grape berries

The concentrations order of major elements in grape berries (K> Ca> Mg> Na) was consistent with the study of Pepi et al. [48](mean concentration of 1688.80, 65.38, 55.42, and 3.77 mg/kg for K, Ca, Mg, and Na) but with significantly higher concentrations found in our study. In comparison with previous research, the concentration ranges of trace elements (Sr, Li, Cd, and Ba) in the "Meili" grape in this study were lower than in other varieties from other regions in China (Sr from 773.20 to 6873.00 μg/kg, Li from 0.25 to 66.60 μg/kg, Cd from 0.10 to 7.40 μg/kg, and Ba from 54.72 to 990.20) [28]. Conversely, Protano et al. [49] observed a lower Sr (mean values 2773 μg/kg) in Sangiovese grape from Tuscany, suggesting that specific elements could distinguish not only the origins but also the grape varieties.

4.1.3. Geographical elemental profile in wine samples

Regarding the concentrations of major elements, our study presented similar magnitudes with many previous reports for wine from other regions around the world [11, 18, 21]. Compared to the concentrations of trace elements in wine samples from other regions in China (mean concentrations were 9975.64, 132.14, 1201.42, 1968.27, 84.9162, 0.43, and 2.85 μg/L for Mn, Cu, Rb, Sr, Li, Cd, and Cs, respectively) [30], Rb and Cs were obviously increased, Cu was slightly increased, whereas Mn, Sr, Li, and Cd were decreased (Table 4).

4.2. Relationships among the soils, grape berries, and wines

The transfer of the elements from the soil to the grape is complicated and mainly determined by the lithological characteristics of parent rock and geochemical outlines of cultivation region, and coupled with the ability of grapevine to uptake the elements and translocate them to leaves and berries [49]. In contrast, the similarity in elemental profiles may well be found between the grapes and the wines, due to the grape chemistry together with the winemaking techniques [20, 23].

Therefore, the influence of the elemental concentrations in vineyard soils on the elemental composition of "Meili" grape berries was determined by Pearson correlation coefficient (r). Only concentrations of K, Li, and Cd present significant correlations between soils and grape berries ($r = 0.66$ for K and Cd, $r = -0.74$ for Li, $p<0.01$) (Figure 2). Moreover, Concerning the accumulation ability of elements in grape berries, the bioconcentration factor (BCF) was evaluated (Suppl. Table 1). The BCF values of most elements are even less than 0.01. These results demonstrated that the concentrations of the elements in grape berries may be strictly controlled by the grapevine rather than by their concentrations in soil, which was in agreement with the results of Protano et al. [49]. In addition, the concentrations of Cd (mean values from 0.22 to 1.70 μg/kg) in grape berries didn't exceed the maximum permissible concentration (<50 μg/kg) according to the Chinese Food Safety Standard (GB2762-2017) [50].

The elemental composition of wine is mainly influenced by the absorption of elements from vineyard soil by vine plant and the winemaking process [20, 23]. The concentrations of six elements (Na, Mg, K, Zn, Li, and Cs) increased slightly after fermentation ($TF>1$) (Suppl. Table 3), probably as a result of extraction from skin and seeds [51, 52]. Additionally, six elemental concentrations (K, Mn, Rb, Sr, Li, and Cs) present significant positive correlation between the wines and the grape berries in this study ($p<0.01$) (Figure 3). These results indicated that although vinification could affect the elemental composition of wine, the primary factor affecting the elemental composition of wine is likely to be the geographical origin, which is consistent with previous reports [23, 52].

4.3. The geographical characteristic elements K, Sr, and Li

The main factors that control the elements uptake by plants from the soil are geochemical, climatic, biological and anthropogenic origin [53]. Therefore, elemental profiling could be reliable method for assessing geographical origin due to the relationship between the elemental composition of soil with that in the wine via the grapes produced in that soil [54]. K, Sr, and Li were observed not only significantly correlated among soil, grape, and wine, but also their accumulation from soil to grape berry showed significant correlation with environmental factors in this study. Moreover, LDA was employed to confirm that these three elements could to be as critical markers to discriminant the provenance of the six regions in China.

Sr has high geochemical mobility and is easily absorbed by all parts of the vine including grapes due to its chemical affinity to Ca [55], then transferred into wine without being altered during the winemaking process [56]. Therefore, Sr contained in wine directly originates from the soil and could be used as a reference to the geographical origin of plants [19]. This also explains the result of our study that the concentrations of Sr show a significant positive correlation between the wines and grape berries (Figure 3d). Besides, the TF values of Sr in grape-wine system were below 1 (Suppl. Table 3) further indicated that Sr was less affected by the winemaking processes [56]. As shown in Figure 4a, the BCF values of Sr showed a significant negative correlation with average relative humidity, reflecting that the transfer of Sr from soil to grape berries was related closely to the climatic conditions [19]. Moreover, numerous studies show a promising perspective for provenance determinations of wine by the elemental and isotopic composition of Sr [11, 18, 19, 26, 49, 57].

Li is neither an essential nor a micronutrient for the vine, still, it plays a vital role in the human body as an effective mood stabilizer [58]. Commonly, the elemental and isotopic Li responds to silicate weathering intensity and could be a weathering tracer [59]. In our study, Li showed a significant negative correlation between soil and grape berries (Figure 2c), suggesting that a higher concentration of Li may inhibit the accumulation of Li in grape berries. This result is similar to the previous research by Ren et al., who found that the Li accumulation of *Apocynum* decreased when the lithium concentration increased to 400 mg/kg [60]. Nevertheless, Li presented significant positive correlation between grape berry and wine (Figure 3e) implied that the element Li of the wine is the result of its presence in the vineyard soil and its uptake by the vine plant [23]. Additionally, the BCF value of Li has a significant negative correlation with temperature and altitude (Figure 4b and c). These results highlight that the geographical and climatic factors predominant influence the uptake of Li by grape from soil. Moreover, Su et al. [30] classified 142 wines from five Chinese regions by Li and the other eight elements. The wines from Shandong in China were effectively differentiated from France by Li and other seven inorganic elements [61]. These results confirmed that Li could be an essential element for identifying the geographical origin of wine in China.

The major element K is essential for a vine plant's health and accumulates in grape berries naturally during the growing season, but also added from the winemaking process such as through potassium metabisulphite [20, 54]. K was significantly different in soil, grape, and wine among six studied regions. Additionally, K was the most abundant element in grape berries and wines, and was second only to that of Fe in the soil (Table 2). Pearson correlation analysis employed and found that K showed significant positive correlations among the soils, grape berries, and wines (Figure 2a and 3a) highlighting that K is important variable related to vineyard soil and grape maturity. Consequently, the present results suggest that K, Sr, and Li are of extraordinary significance for geographical origin traceability of wine in the studied regions.

5. Conclusions

In summary, our study observed diverse patterns of the fifteen elements accumulation in soil, grape berries, and wines from six regions in China. All the determined minerals were under the maximum limit admitted (OIV-MA-C1-01 2011, GB2762-2017,

GB15618-2018) [47, 50, 62]. It is the first study to evaluate the relationships of major and trace elements in the system soil-grape-wine combined with bioaccumulation factors and environmental factors in China. There were good correlations among soils, grape berries, and wines. The differences in elemental profiles of wines from different Chinese regions are mainly due to the diverse soil geochemistry and the elemental selective absorption of grapevine from soil. Three elements K, Sr, and Li exhibited their potential as indicators for Chinese geographical origin identification. Nevertheless, more regions, grape varieties, and vintages must be analyzed in order to consolidate this conclusion.

Author Contributions: Conceptualization, X.H.; methodology, X.H.; software, F.G.; formal analysis, F.G.; data curation, H.W.; writing—original draft preparation, X.H.; writing—review and editing, F.G., L.Z.; visualization, Y.S.; supervision, H.W.; project administration, H.W.; funding acquisition, H.L. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the National Key Research and Development Project of China (No. 2019YFD1002500) and Shaanxi Provincial Key Research and Development Projects (No. 2020ZDLNY07-08).

Acknowledgments: The authors are thankful to the Food Inspection and Quarantine Center of Shenzhen Customs in China for providing the testing equipment and other assistance.

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

References

1. Angerosa, F.; Breas, O.; Contento, S.; Guillou, C.; Reniero, F.; Sada, E. Application of stable isotope ratio analysis to the characterization of the geographical origin of olive oils. J. Agric. Food Chem. 1999, 47, 1013-1017.
2. Petrini, R.; Sansone, L.; Slejko, F.F.; Buccianti, A.; Marcuzzo, P.; Tomasi, D. The (87)Sr/(86)Sr strontium isotopic systematics applied to Glera vineyards: a tracer for the geographical origin of the Prosecco. Food Chem. 2015, 170, 138-144.
3. Versari, A.; Laurie, V.F.; Ricci, A.; Laghi, L.; Parpinello, G.P. Progress in authentication, typification and traceability of grapes and wines by chemometric approaches. Food Research International 2014, 60, 2-18.
4. OIV (2021). Oiv state of the world-vitivinicultural-sector in 2020. OIV.
5. Picque, D.; Cattenoz, T.; Corrieu, G.; Berger, J.L. Discrimination of red wines according to their geographical origin and vintage year by the use of mid-infrared spectroscopy. Sciences Des Aliments 2005, 25, 207-220.
6. Geana, E. I.; Popescu, R.; Costinel, D.; Dinca, O.R.; Ionete, R.; Stefanescu, E.I.; Artem, V.; Bala, C. Classification of red wines using suitable markers coupled with multivariate statistic analysis." Food Chem. 2016, 192, 1015-1024.
7. Basalekou, M., Pappas, C. Tarantilis, P. Kotseridis, Y. Kallithraka, S. Wine authentication with Fourier Transform Infrared Spectroscopy: a feasibility study on variety, type of barrel wood and ageing time classification. International Journal of Food Science and Technology 2017, 52, 1307-1313.
8. Louw, L.; Roux, K.; Tredoux, A.; Tomic, O.; Naes, T.; Nieuwoudt, H.H.; van Rensburg, P. Characterization of selected south african young cultivar wines using FTMIR spectroscopy, gas chromatography, and multivariate data analysis. Journal of Agricultural and Food Chem. 2009, 57, 2623-2632.
9. Pisano, P.L.; Silva, M.F.; and Olivieri, A.C. Anthocyanins as markers for the classification of Argentinean wines according to botanical and geographical origin. Chemometric modeling of liquid chromatography–mass spectrometry data. Food Chem. 2015, 175, 174-180.
10. Vilanova, M., Rodriguez, I.; Canosa, P. Otero, I.; Gamero, E.; Moreno, D.; Talaverano, I.; Valdes, E. Variability in chemical composition of *Vitis vinifera* cv Mencia from different geographic areas and vintages in Ribeira Sacra (NW Spain). Food Chem. 2015, 169; 187-196.
11. Pérez-Álvarez, E.P.; Garcia, R.; Barrulas, P.; Dias, C.; Cabrita, M.J.; Garde-Cerdán, T. Classification of wines according to several factors by ICP-MS multi-element analysis. Food Chem. 2019, 270, 273-280.
12. Wu, H.; Tian, L.; Chen, B.; Jin, B.; Tian, B.; Xie, L.; Rogers, K.M.; Lin, G. Verification of imported red wine origin into China using multi isotope and elemental analyses. Food Chem. 2019, 301, 125137.
13. Luykx, D.M.A.M.; van Ruth, S. M. An overview of analytical methods for determining the geographical origin of food products. Food Chemistry 2008, 107, 897-911.
14. Drivelos, S.A. and Georgiou, C.A. Multi-element and multi-isotope-ratio analysis to determine the geographical origin of foods in the European Union." TrAC-Trends in Analytical Chem. 2012, 40, 38-51.
15. Georgiou, C.A.; Danezis, G.P. Advanced Mass Spectrometry for Food Safety and Quality. Comprehensive Analytical Chemistry. Y. Picó, 2015 Elsever: 131-243.
16. Danezis, G.P., Tsagkaris, A.S.; Camin, F.; Brusic, V.; Georgiou, C.A. Food authentication: Techniques, trends & emerging approaches. TrAC-Trends in Analytical Chem. 2016, 85,123-132.

17. Kokkinofta, R.; Fotakis, C.; Zervou, M.; Zoumpoulakis, P.; Savvidou, C.; Poulli, K.; Louka, C.; Economidou, N.; Tzioni, E.; Damianou, K.; Loupasaki, S.; Kefalas, P. Isotopic and elemental authenticity markers: a case study on Cypriot wines. Food Analytical Methods 2017, 10, 3902-3913.
18. Pepi, S.; Grisenti, P.; Sansone, L.; Chicca, M.; Vaccaro, C. Chemical elements as fingerprints of geographical origin in cultivars of *Vitis vinifera* L. raised on the same SO4 rootstock." Environ Sci Pollut Res Int 2018, 25, 490-506.
19. Epova, E. N.; Berail, S.; Seby, F.; Vacchina, V.; Bareille, G.; Medina, B.; Sarthou, L.; Donard, O.F.X. Strontium elemental and isotopic signatures of Bordeaux wines for authenticity and geographical origin assessment. Food Chem. 2019, 294, 35-45.
20. Pohl, P. What do metals tell us about wine? Trends in Analytical Chemistry 2007, 26, 941-949.
21. Pasvanka, K.; Tzachristas, A.; Kostakis, M.; Thomaidis, N.; Proestos, C. Geographic characterization of Greek wine by inductively coupled plasma–mass spectrometry macroelemental analysis. Analytical Letters 2019, 52, 2741-2750.
22. Shimizu, H.; Akamatsu, F.; Kamada, A.; Koyama, K.; Okuda, M.; Fukuda, H.; Iwashita, K.; Goto-Yamamoto, N. Discrimination of wine from grape cultivated in Japan, imported wine, and others by multi-elemental analysis. J Biosci Bioeng 2018, 125, 413-418.
23. Hopfer, H.; Nelson, J.; Collins, T.S.; Heymann, H.; Ebeler, S.E. The combined impact of vineyard origin and processing winery on the elemental profile of red wines. Food Chem. 2015, 172, 486-496.
24. Coetzee, P. P.; van Jaarsveld, F. P.; Vanhaecke, F. Intraregional classification of wine via ICP-MS elemental fingerprinting. Food Chem. 2014, 164, 485-492.
25. Martin, A.E.; Watling, R.J. Lee, G.S. The multi-element determination and regional discrimination of Australian wines. Food Chem. 2012, 133, 1081-1089.
26. Geana, I.; Iordache, A.; Ionete, R.; Marinescu, A.; Ranca, A.; Culea, M. Geographical origin identification of Romanian wines by ICP-MS elemental analysis. Food Chem. 2013, 138, 1125-1134.
27. Šelih, V.S.; Šala, M.; Drgan, V. Multi-element analysis of wines by ICP-MS and ICP-OES and their classification according to geographical origin in Slovenia. Food Chem. 2014, 153, 414-423.
28. Zou, J.F.; Peng, Z.X.; Du, H.J.; Duan, C.Q.; Reeves, M.J.; Pan, Q.H. Elemental patterns of wines, grapes, and vineyard soils from Chinese wine-producing regions and their association. American Journal of Enology and Viticulture 2012, 63, 232-240.
29. Fan, S.X.; Zhong, Q.D.; Gao, H.B.; Wang, D.B.; Li, G.H.; Huang, Z.B. Elemental profile and oxygen isotope ratio (delta(18)O) for verifying the geographical origin of Chinese wines. J Food Drug Anal. 2018, 26, 1033-1044.
30. Su, Y.; Gao, J.; Zhao, Y.; Wen H.; Zhang, J.; Zhang, A.; Yuan, C. Geographical origin classification of chinese wines based on carbon and oxygen stable isotopes and elemental profiles. J Food Prot 2020, 83, 1323-1334.
31. Zhang, Z.W.; Wang, H.; Fang, Y.L.; Xi, Z.M.; Li, H. A new high quality wine-grape cultivar 'Meili' with disease resisitance. Acta Horticulturae Sinica 2013, 40, 1611–1612.
32. Fang, Y.L.; Song, S.R.; Zhang, Y.F.; He, J.L.; Chen, S.X. Relatioship of *Downy Mildw* Resistance with Leaf POD and PPO activities of different grapevine varieties. Act a Bot. Boreal 2007, 27, 0392-0395.
33. Peng, C.T.; Liu, H.; Mou, H.; Hu, K.; An, R.; Tao, Y.S. Study on contribution of aroma components of 'Meili' wine variety. Journal of Chinese Institute of Food Science and Technology 2015, 15, 230-239.
34. Shu, T.T.; Li, Y.; Li, N.N.; Liu, X.; Duan, Q.; Li, H.; Wang, H. Adaptability and quality of wine grape Meili in different climate zones. China Brewing 2018, 37, 95-100.
35. Lecourt, J.; Lauvergeat, V.; Ollat, N.; Vivin, P.; Cookson, S.J. Shoot and root ionome responses to nitrate supply in grafted grapevines are rootstock genotype dependent. Australian Journal of Grape and Wine Research 2015, 21, 311-318.
36. Maurizio, Z.; Alessandra, G.; Matteo, G.; Alberto, V.; Giulia, P.M.; Luigi, B.; Stefano, P. Vegetative, physiological and nutritional behavior of new grapevine rootstocks in response to different nitrogen supply. Scientia Horticulturae 2016, 202, 99-106.
37. Pisciotta, A.; Tutone, L.; Saiano, F. Distribution of YLOID in soil-grapevine system (*Vitis vinifera* L.) as tool for geographical characterization of agro-food products. A two years case study on different grafting combinations. Food Chem. 2015, 221, 1214-1220.
38. Rodrigues, S.M.; Marta, O.; Alves, A.A.; Coimbra, J.; Coimbra, M.A.; Pereira, E.; Duarte, A.C. Elemental analysis for categorization of wines and authentication of their certified brand of origin. Journal of Food Composition and Analysis 2011, 24, 548-562.
39. Ehlken, S.; Kirchner, G. Environental processes affecting plant root uptake of radioactive trace elements and variability of transfer factor data: a review. Journal of Environmental Radioactivity 2002, 58, 97-112.
40. Montanaro, G.; Dichio, B.; Lang, A.; Mininni, A.N.; and Xiloyannis, C. Fruit calcium accumulation coupled and uncoupled from its transpiration in kiwifruit. J Plant Physiol 2015, 181, 67-74.
41. Boechat, C.L.; Duarte, L. de S.L.; de Sena, A.F.S.; de Nascimento, C.W.A.; de Silva, Y.J.A.B.; de Silva, Y.J.A.B.; Brito, A.C.C.; Saraiva, P.C. Background concentrations and quality reference values for potentially toxic elements in soils of Piaui state, Brazil. Environ Monit Assess 2020, 192, 723.
42. Shi, W.; Lv, D.Q.; Emteryd, O. Relationship between soil texture and nitrate distribution and accumulation in three types of soil profile in Shaanxi. Plant Nutrition and Fertilizer Science 2005, 11, 435-441.
43. Pang, J.L.; Huang, C.C.; Zhang, X.; Zhou, Z.X.; Zha, X.C. Micromorphological features of the cultivated soil and anthropogenic forest soil at Bailuyuan site, Shaanxi province. Acta Pedologica Sinica 2007, 44, 792-800.

44. Zhi, Y.B.; Yang, C.; Li, H.L.; Zang, H.L.; Hua, Y.P.; Zhao, K.; Lu, Z.Y.; Hong, G.; Wang Z.L.; Wang, Q. The bioclimatology and photosynthetic characteristics for the ex-situ conservation of the endemic relict shrub Tetraena mongolica. Journal of Desert Research 2014, 34,88-97.
45. Zhang, B.X. Introduction of goldfinger grape in Henan province and its cultivation techniques. Journal of Shanxi Fruit Trees 2015, 1: 21-22.
46. Cui, C.W.; Ding, J.X.; Li, H.; Zhang, L.; Duan, Q.; Wang, H. Study on introduction and cultivation of 'Beibinghong' in Heyang Shaanxi. Northern Horticulture 2015, 06, 36-39.
47. GB15618-2018 (2018). Soil environmental quality Risk control standard for soil contamination of agricultural land. Environmental Science Press of China, Beijing.
48. Pepi, S.; Vaccaro, C. Geochemical fingerprints of ''Prosecco'' wine based on major and trace elements. Environ Geochem Health 2018, 40, 833-847.
49. Protano, G.; Rossi, S. Relationship between soil geochemistry and grape composition in Tuscany (Italy). Journal of Plant Nutrition and Soil Science 2014, 177, 500-508.
50. GB2762-2017 (2017). Chinese Food Safety Standard: Maximum Limit of Contaminants in Food.
51. Anjos, M.J.; Lopes, R.T.; de Jesus, E.F.O.; Moreira, S.; Barroso, R.C.; Castro, C. R. F. Trace elements determination in red and white wines using total-reflection Xray fluorescence. Spectrochimica Acta B 2003, 58, 2227-2232.
52. Shimizu, H.; Akamatsu, F.; Kamada, A.; Koyama, K.; Iwashita, K.; Goto-Yamamoto, N. Variation in the mineral composition of wine produced using different winemaking techniques. J Biosci Bioeng 2020, 130, 166-172.
53. Kabata-Pendias, A. Soil–plant transfer of trace elements—an environmental issue. Geoderma 2004, 122, 143-149.
54. 54. Ranaweera, R.K.R.; Gilmore, A.M.; Capone, D.L.; Bastian, S.E.P.; Jeffery, D.W. Authentication of the geographical origin of Australian Cabernet Sauvignon wines using spectrofluorometric and multi-element analyses with multivariate statistical modelling. Food Chem. 2021, 335, 127592.
55. De Vos, W., Demetriades, K.; Marsina, K.; Ottesen, R.T.; Reeder, S.; Pirc, S.; Salminen R.; Tarvainen, T. Comparison of elements in all sample media, general comments and conclusion. Geochemical Atlas of Europe, Part 2. W. De Vos and T. Tarvainen. Espoo, Finland, Geochemical Survey of Finland, 2006, 49-425.
56. Almeida, C.M.R.; Vasconcelos, M.T.S.D. Does the winemaking process influence the wine $^{87}Sr/^{86}Sr$? A case study. Food Chem. 2004, 85, 7-12.
57. Braschi, E.; Marchionni, S.; Priori, S.; Casalini, M.; Tommasini, S.; Natarelli, L.; Buccianti, A.; Bucelli, P.E.; Costantini, A.C.; Conticelli, S. Tracing the $^{87}Sr/^{86}Sr$ from rocks and soils to vine and wine: An experimental study on geologic and pedologic characterisation of vineyards using radiogenic isotope of heavy elements. Science of the Total Environment 2018, 628-629, 1317-1327.
58. Del Matto, L.; Muscas, M.; Murru, A.; Verdolini, N.; Anmella, G.; Fico, G.; Corponi, F.; Carvalho, A.F.; Samalin, L.; Carpiniello, B.; Fagiolini, A.; Vieta, E.; Pacchiarotti, I. Lithium and suicide prevention in mood disorders and in the general population: A systematic review. Neurosci Biobehav Rev. 2020, 116, 142-153.
59. Pogge von Strandmann, P.A.E.; Opfergelt, S.; Lai, Y.J.; Sigfusson, B.; Gislason, S.R.; Burton, K.W. Lithium, magnesium and silicon isotope behaviour accompanying weathering in a basaltic soil and pore water profile in Iceland. Earth and Planetary Science Letters 2012, 339-340, 11-23.
60. Ren, J.; Tian, C.Y. Effects of lithium concentration treatments on growth of apocynum seedling and its lithium accumulation. Arid Zone Research 2014, 31, 313-316.
61. Xiong, X.; Liu, J.F.; Cai, Z.F.; Liang, X.X.; Zhang, J.H.; Zhang, P.X.; Zhou, Y.L.; Lin, H.H. Trace of geographical origin of wine by principal component analysis. Journal of Food Safety and Quality 2020, 11, 5477-5484.
62. OIV-MA-C1-01. Maximum acceptable limits of various substances contained in wine. 2011.