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Geochemical fingerprints of "Prosecco" wine based on major and trace elements

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Abstract:	The terroir can be defined as interactive ecosystem that includes climate, geology, soil and grapevine, and it is used to explain the hierarchy of high-quality of wine. In order to understand the terroir functions it is necessary to analyse the interactions among the geology, soil and wine. To define a geochemical fingerprint, the relationship between geochemistry of vineyard soil and chemical composition of wine from Veneto Italian Region, was studied. The vineyards tested belonged to four distinct wineries located in the Veneto alluvial plain, included in the Controlled Designation of Origin (DOC) area of Prosecco. We investigated the relationship between major and trace elements in soil and their concentrations in Prosecco wine according to geographic origin. The detection of chemical composition in soil and wine were analysed by inductively coupled plasma-mass spectrometry (ICP-MS), and data were elaborated by non-parametric test and multivariate statistics LDA (Linear Discrimination Analysis). The geochemical and statistical analyses allowed to discriminate the vineyard soils according to geo-lithological characteristics of each area and to identify the geochemical "Prosecco" fingerprints, useful against fraudulent use of DOC wine labels
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Dear Sirs,

we would like to submit to Environmental Geochemistry and Health the manuscript "Geochemical fingerprints of "Prosecco" wine based on major and trace elements" by Pepi and Vaccaro.

The authors declare that the work has not been previously published and has not been submitted elsewhere for publication.

Best regards,

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Geochemical fingerprints of "Prosecco" wine based on major and trace elements

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Abstract

The terroir can be defined as interactive ecosystem that includes climate, geology, soil and grapevine, and it is used to explain the hierarchy of high-quality of wine. In order to understand the terroir functions it is necessary to analyse the interactions among the geology, soil and wine. To define a geochemical fingerprint, the relationship between geochemistry of vineyard soil and chemical composition of wine from Veneto Italian Region, was studied. The vineyards tested belonged to four distinct wineries located in the Veneto alluvial plain, included in the Controlled Designation of Origin (DOC) area of Prosecco. We investigated the relationship between major and trace elements in soil and their concentrations in Prosecco wine according to geographic origin. The detection of chemical composition in soil and wine were analysed by inductively coupled plasma-mass spectrometry (ICP-MS), and data were elaborated by non-parametric test and multivariate statistics LDA (Linear Discrimination Analysis). The geochemical and statistical analyses allowed to discriminate the vineyard soils according to geo-lithological characteristics of each area and to identify the geochemical "Prosecco" fingerprints, useful against fraudulent use of DOC wine labels.

Keywords: ICP-MS, Veneto, Glera, LDA, Major and trace elements

Introduction

The French word “terroir”, literally meaning “land” or “soil”, is used in winemaking as a geographical way to indicate the unique environment and farming practices characterizing a wine producing region (Wilson 1998; Van Leeuwen and Seguin 2006; Tomasi et al. 2010; Cadot et al. 2012; Costantini et al. 2012; Dougherty 2012). After the first historic French certification “Appellation d’Origine Contrôlée’’ (AOP), other wine producing countries have accepted the concept of “terroir” and encoded it by local laws: for example, in Italy wines are classified according to “Denominazione di Origine Controllata” (Controlled Designation of Origin, DOC), and in United States as “American Viticultural Area” (AVA) (Tomasi et al. 2010; Dougherty 2012; Lenglet 2014). From a geographic point of view, the “terroir” generally corresponds to the boundaries of specific geo-litological regions. For example, in France the AOP wines “Dry” champagne, “Premier Cru” red and “Commune” belong to specific geological outlines, respectively the formations “Chalk” (Upper Cretaceous), “Dalle nacrèe” (pearly flagstone, Middle Jurassic) and “Digonella” (marly limestone, Middle Jurassic) (Wilson 1998; Huggett 2006). In Italy, the DOC wines “Negroamaro” and “Chianti” respectively belong to the “Murge Plateau” (limestone and dolostones, Cretaceous) (Pepi et al. 2016) and Chianti geological terroir (fluvial deposits, Pliocene). Besides climate and viticultural practices, wine properties may reflect the soil geochemistry: for example, in Italy, Piedmont marls characterize the “Nebbiolo” wine and in France the schists characterize the “Chardonnay” ones. Wine properties may also be affected by the bioavailability of inorganic compounds in soil: the concentration of elements such as Al and Fe may change during wine making processes because of the addition of bentonite as wine clarifier (Catarino et al. 2008). However, elements that do not change during wine making, such as Si, Mg, Ti, Mn and Mo, could be good markers for the geographical territoriality (Marengo and Aceto 2003; Aceto et al. 2013). For example, wines from two different areas of Valencia (Spain) were discriminated on the basis of their concentration of Li and Mg (Gonzalvez et al. 2000) and those from three regions of Southern

Italy (Basilicata, Calabria and Sicily) on their concentration of Li and Rb (Galgano et al. 2008). Recent studies dealt with geochemical characterization of grape berries associated to a specific geographical environment for prevention of fraudulent labelling (Petrini et al. 2015; Pepi et al. 2016b; Pepi et al. 2017; D'Antone et al. 2017). The concentration of major, trace and rare earth elements has been studied by inductively coupled plasma mass (ICP-MS) and inductively coupled plasma optical emission spectrometry (ICP-OES) (Gonzalez et al. 2008; De La Guardia and Gonzalvez 2013) in wines (Galgano et al. 2008; Fabani et al. 2010; Aceto et al. 2013; Marchionni et al. 2013; Kristensen et al. 2016;) and in some cases it was related to terroir (Di Paola-Naranjo et al. 2011; Cugnetto et al. 2014; Mercurio et al. 2014). Other studies concerned the concentration of trace and rare earth elements in grapes (Censi et al. 2014; Pisciotta et al. 2017; D'Antone et al. 2017) and these data were related to the terroir of grape production (Pepi et al. 2016b; Pepi et al. 2017). Statistical approaches have shown that it is possible to characterize a chemical fingerprint of soil able to identify the geological and geographic origin of wines produced in a given area (Almeida and Vasconcelos 2004; Coetzee et al. 2005; Álvarez et al. 2007; Cugnetto et al. 2014; Pii et al. 2017). Besides chemical elements, the isotope ratios of 87Sr/86Sr have also been employed as tracers of the geological substrate to identify the wine production area (Di Paola-Naranjo et al. 2011; Marchionni et al. 2013; Petrini et al., 2015). All the above geological and geochemical characterizations are presently accepted as good indicators of geographical origin of fine wines and have been used to prevent falsification and fraudulent use of denomination labels (Versari et al. 2014).

According the disciplinary of Controlled Designation of Origin (DOC), the most renowned Italian sparkling wine, "Prosecco", must be produced from grapes raised only in some provinces of the regions Veneto and Friuli-Venezia Giulia (Tomasi et al. 2010). The "Prosecco" should be made exclusively from grapes of the cultivar "Glera", but in its production a maximum of 15% of other grapes may be used, belonging only to specific cultivars stated in the disciplinary (Tomasi et al. 2010).

The purpose of this study was to establish geochemical fingerprints of the “Prosecco” produced only with “Glera” grapes from the Italian Region Veneto, identifying the relationships between the concentration of major and trace elements in soil samples and those in wine samples determined by ICP-MS. The geochemical “Prosecco” fingerprint would be able to discriminate the vineyard soils according to geo-lithological characteristics of each area and prevent falsification and fraudulent use of “Prosecco” wine label.

Material and methods

Geological setting and sampling

The samples analysed belonged to four vineyards respectively located in the areas Bagnoli di Sopra, Braga, Broscagin and Peraro in the Veneto Region, Northern Italy (Fig. 1). The common geological substrate of these areas is composed by recent fine sediments from Pleistocene to Holocene and the climate of the sampling area is characterized by low winds from East and North-East and average annual temperature 20 °C. Rainfalls are distributed along the year with averages 800 and 1100 mm/y, respectively in the low and high alluvial plain, and 2000 mm/y on Prealps (Barbi et al. 2012).

Soil sampling was carried out in the four areas by an Edelman auger (Eijkelkamp Soil & Water, Giesbeek, The Netherlands). For each sampling area, eight soil samples about 1500 g each were collected at the depth of 60 cm and at 50 cm of distance from each plant: each sample was collected in triplicate. Wine samples were collected directly from wine bottled by producers (eight bottles from each area), selecting only wine exclusively produced with Glera grapes in the year 2014. Samples were collected from bottles discarding the first 50 ml of liquid and pouring 100 mL in 42 x 90 mm Teflon containers (VWR International, Milan, Italy): wine samples from each bottle were collected and analysed in triplicate.

Sample treatments

Soil samples were dried at 105 °C for 24 h to eliminate the hygroscopic water, grounded in a mortar grinder (Laarmann LMMG 100, Roermond, The Netherlands) and dried at 500 °C to eliminate the organic matter. An amount of 0.20 g of powder was placed in a 50-mL Teflon digestion vessel, 43 x 60 mm (VWR International), adding 3 mL of HNO_3 (65% in distilled water, Suprapur®, Merck KGaA, Darmstadt, Germany) and 6 mL of HF (40% in distilled water, Suprapur®, Merck KGaA). The mixture was heated on a hotplate at 180-190 °C for 4-5 hours until complete drying, 3 mL of HNO_3 and 3 mL of HF were added to the dried mixture, which was heated for 3 hours. The dry residue was resuspended in 4 mL of HNO_3 and heated until complete drying. Finally, the dry residue was resuspended in 2 mL of HNO_3.

An amount of 4 g of wine was accurately weighed in a 50-mL Teflon digestion vessel (VWR International), adding 5 ml of HNO_3 (65% in distilled water, Suprapur®, Merck KGaA) and 2 ml of H_2O_2 (37% in distilled water, Suprapur®, Merck KGaA). Each sample was heated at 110-140 °C for 3 hours until complete drying and resuspended in 2 mL HNO_3.

The final solutions of soil and wine samples were transferred to plastic flasks (VWR International) and made up to 100 mL with highly purified Milli-Q® water. An internal element standard composed of Rh, Re, In and Bi for soil samples and one composed of Rh and Re for wine samples was added to each solution to a final concentration of 10 ppb.

Analytical determinations and statistical analysis

Major and trace elements in soil and wine samples were determined by inductively coupled plasma-mass spectrometry (ICP-MS) using a Thermo Electron Corporation X series spectrometer (Thermo Fisher Scientific, Waltham, Massachusetts). The elements determined were Al, As, B, Ba, Ca, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Rb, Sb, Se, Sn, Sr, Ti, Tl, V and Zn. The detection limits were 1-10 ppb for Al, Ca and Fe, 0.1-1 for Mg, K and Na, and less than 0.1 ppb for all other elements. The accuracy of the analysis of soil samples was checked by NIST 2709 and USGS GXR-2 certified reference materials and was generally lower than 15% for all elements. For wine samples, the standard reference materials was SRM 1547 – Peach Leaves (National Institute of Standards and Technology, Gaithersburg, Maryland).

The Kruskal-Wallis non-parametric test (with post-hoc Dunn's test) was used to detect differences among groups in all data from soil and wine samples. Linear discriminant analysis (LDA) was chosen as multivariate analysis for all ICP-MS data as previously described (Rencher 2002; Pepi et al., 2017). All analyses were carried out by the software XLSTAT (Version 2015.5.02, Addinsoft, Paris, France).

Result and discussions

Geochemical characterization of soil samples

Major and trace elements in soil samples collected from the four vineyards of Bagnoli di Sopra, Braga, Broscagin and Peraro are reported in Table. 1. Statistically significant differences ($p<0.05$) were obtained for all major and trace elements (expressed as mg/kg) except for Co, K, Sb, Se, Ti, Tl and Zn. In all vineyards, the major element with the highest concentration was Al, followed by Ca, Fe, Mg and Na, and the trace element with the highest concentration was Ba, followed by Sr, Rb, V, Li and Cr.

Bivariate plots of major elements versus trace elements were used to identify the mineralogical assemblages in soil composition (Fig. 2). A significant positive correlation ($R^2 = 0.94$) was detected for Al versus Rb in Broscagin and Peraro vineyards, but the same elements showed a significant negative correlation ($R^2 = 0.50$) in Bagnoli di Sopra (Fig. 2a): these data suggest the presence of clay minerals in soils of Broscagin and Peraro vineyards (Pepi et al. 2017). Significant positive correlations were detected in all vineyards for Fe versus V (Fig. 2b) and Cr versus Ni (Fig. 2c) except for Cr versus Ni in Bagnoli di Sopra and Broscagin ($R^2 = 0.40$ and $R^2 = 0.34$, respectively).

The significant positive correlations of Fe versus V suggest the presence of clay minerals and Al/Fe hydrous-oxides in alluvial deposits (Pepi et al. 2017), while those of Cr versus Ni suggest the presence of chlorite and mafic minerals in alluvial deposits (Huang et al. 2012; Petrini et al. 2015; Pepi et al. 2017).

In order to analyse in more detail the distribution of major and trace elements in soils of all vineyards, box plots of the concentrations shown in Table 1 were represented in Figure 3 and Figure 4, respectively for major and trace elements. In Peraro and Braga vineyards, a higher concentration of Al was detected in comparison to Bagnoli di Sopra and Broscagin (Fig. 3a), revealing a higher presence of phyllosilicates minerals in the former two vineyards and the origin of their soil from alluvial sediments (Huang et al. 2012). The higher concentration of Ca and Mg in Broscagin and Bagnoli di Sopra in comparison to Braga and Peraro (Fig. 3b, c) suggests the presence of calcite and dolomite minerals, according to the results of a previous study (Petrini et al. 2014). The highest concentration of Na detected was detected in Peraro, probably because the soil of this vineyard is richer in silicate and clay minerals (Huang et al. 2012; Petrini et al. 2014; Pepi et al. 2017).

Concerning trace elements, As shows the highest concentration in Bagnoli di Sopra (Fig. 4a). The concentration of As is thought to be related to Fe hydroxide and phyllosilicate minerals (Hooda 2010). The elements Ba and B respectively show a higher concentration in Braga (Fig. 4b) and Peraro (Fig. 4c) in comparison to the other two vineyards: the affinity of these two elements suggest the presence of illite and montmorillonite minerals and of organic matter in these two soils (Hooda 2010; Kabata-Pendias 2011). The element Cu shows higher concentrations in Broscagin and Peraro (Fig. 4d) in comparison to Bagnoli di Sopra and Braga. Generally, Cu is rather non-mobile and tends to accumulate in the upper few centimeters of soil, thus its higher concentration suggest an association with oxyhydroxides of Mn, Fe and Al, and with clay minerals (Hooda 2010; Komárek et al. 2008; Fernández-Calviño et al. 2008; Kabata-Pendias 2011). The highest concentrations of Cr, Ni and Pb were found in Peraro (Fig. 4e,f,g) in comparison to all other vineyards. These three elements, usually associated in femic and clay minerals (Hooda 2010; Kabata-Pendias 2011), suggest the presence of these minerals in Peraro soil. It is known that Pb is common in minerals because it may substitute for K, Sr Ba and Ca, and also because it is used in phosphatic fertilizers and in spray pesticides (Hooda 2010). The elements Rb and Sn also show the highest concentrations in Peraro (Fig. 4h,i) in comparison to all other vineyards. In soil, Rb is mainly linked to the parent rock, to alluvial sediments and micaceous clays (Kabata-Pendias 2004; Kabata-Pendias 2011; Petrini et al. 2015; Pepi et al. 2017), while Sn is linked to the clay fraction and metal oxides, because its mobility is similar to that of Al and Fe (Kabata-Pendias 2011). The Peraro soil therefore appears richer in clay minerals and metal oxides.

Generally, the four vineyard soils examined showed a heterogeneous set of concentrations of major and trace elements, changing according to geographical origin, thus useful as geochemical fingerprints of the vineyards.

Chemical composition of wine samples

The chemical compositions of wine samples collected in the four vineyards are reported in Table 2. More than half of the element concentrations showed statistically significant differences ($p < 0.05$) an the highest values of major elements in wine samples were respectively K, Ca and Mg in all vineyards. Concerning trace elements, the highest values were respectively Ni, Rb and Ti (Table 2). The major elements Ca, K, Mg and Na in wine samples from the four vineyards were plotted as box plots in Figure 5. The element Ca showed higher values in wine samples from Braga and Broscagin, in comparison to Bagnoli di Sopra and Peraro (Fig.5a). Besides being a major element, Ca is a natural component of grape and commonly employed in oenological treatments of deacidification by addition of $CaCO_3$ or $CaSO_4$ which increase the concentration of Ca in wine samples (Scollary 1997; Álvarez et al. 2007; Pepi et al. 2016a; Pepi et al. 2017). The element K showed higher values in Bagnoli di Sopra and Broscagin in comparison to Braga and Peraro (Fig. 5b). As Ca, K is an essential element in grape and a component of agricultural treatments, linked to the use of pesticides and fertilizers (Kallithraka et al. 2001; Álvarez et al. 2007; Pohl 2007; Rodrigues et al. 2011). The values of Mg in wine samples were slightly lower in Broscagin and Peraro in comparison to Bagnoli di Sopra and Braga (Fig. 5c). The higher concentration of Mg in the examined wine samples was probably related to its natural content in grape berries of *Vitis vinifera* cv. Glera, as previously described (Pepi et al. 2017). The concentration of Na was lower in wine samples from Peraro than in those from all other vineyards (Fig. 5d): these values may be affected by geochemical composition of the irrigation water, of agronomy practises and wine processing techniques (Pohl 2007).

The box plots of trace elements shown in Figure 6 reveal that higher levels of B, Li, Mn, Pb, Rb and Ti and lower levels of Cu, Sn and Sr were observed in Bagnoli di Sopra in comparison to all other vineyards.

All these trace elements are in various ways connected to agricultural practices and winemaking processes (Anjos et al. 2003; Rodrigues et al. 2011; Vrček et al. 2011). The elements B, Cu and Li (Fig. 6a,b,c) are essential nutrients for grapevine and linked to common fertilizing practises (Rodrigues et al. 2011; Fregoni, 2013). The concentrations of Mn and Pb are also connected to fungicide addition and contact with machinery (Álvarez et al. 2007; Vrček et al. 2011) and those of Rb, Sn, Sr and Ti are linked to the use of bentonite to clarify the wine (Pohl 2007). Furthermore, the concentrations of Sn and Ti may increase because of contact with stainless steel containers (Anjos et al. 2003; Almeida and Vasconcelos 2004; Rodrigues et al. 2011).

Overall, all data of major and trace elements in wine samples from the four vineyards appear related not only to geographical origin but also to winemaking processes.

Geochemical correlations in soil and wine samples

The concentration values of major and trace elements in soil and wine samples were compared among the four vineyards. Only B and Sr showed a signification correlation in soil and wine samples (respectively $R^2>0.65$ in soil and $R^2>0.67$ in wine) (Fig. 7). The significant positive correlation of B versus Sr in soil samples could be related to illites, K-montmorillonites or organic matter, which may also influence the mobility and availability of these two elements in soil (Fig. 7a). The element B may be entrapped in the clay lattice when exchanging for Al^{3-} or Si^{4-} (Kabata-Pendias 2011), and it is also an essential micronutrient for plant growth and development for its key role in carbohydrate and cell wall metabolism (Kabata-Pendias 2011). Since Sr is known to be interchangeable with Ca, its uptake may be increased by Mg and probably by B (Takeda et al. 2005; Kabata-Pendias 2011).

As previously mentioned, the significant positive correlation of B versus Sr in wine samples may be linked to agricultural practices and winemaking processes (Fig. 7b). Indeed, winemakers have observed an improvement in white wine quality resulting from proper clarification based on bentonite (Ribereau-Gayon et al. 2005; Pohl 2007).

Previous data on Sr obtained by 87Sr/86Sr isotopes and ICP-MS in soil and grape samples from vineyards of the Veneto Region (Petrini et al. 2014; Pepi et al. 2017) support the results obtained in this study for B versus Sr in the four studied vineyards.

Multivariate analysis by LDA in soil and wine samples

The Linear Discriminant Analysis (LDA) was used to identify possible geochemical differences due to geographical origin. Stepwise linear LDA using a Wilks Lambda test ($p< 0.01$) and an F-statistic factor (Rencher 2002) was applied to all data of major and trace elements in soil and wine samples from the four vineyards examined (Tables 1 and 2), by the software XLSTAT. Among all functions calculated by the program, two were chosen as best discriminating functions among all data sets (Rencher 2002). Both discriminating functions were associated to the values of major and trace elements. For soil samples, the plot of the first discriminant function (F1) against that of the second one (F2) is shown in Fig. 8a. The LDA analysis was able to discriminate the soil samples according to their geographical origin, with a validation of 96.88%, confirming that it was possible to identify each vineyard in relation to its location. The highest discrimination among soil samples was linked to F1, in which the elements selected by the forward stepwise process ($p<0.01$) for the discriminant plot are B, Ca, Cr, Cu, Mg, Mo, Mn, Rb, Sb and Sr.

For wine samples, the plot of F1 versus F2 is shown in Fig. 8b. The LDA analysis was able to discriminate the wine samples according to their geographical origin, with a validation of 93.75%. As in Fig. 9a, the highest discrimination among wine samples was linked to F1 and the elements selected by the forward stepwise process ($p<0.01$) for the discriminant plot were B, Ca, Mo, Sb, Sn and Sr.

All the above data confirmed that each one of the four vineyards could be discriminated by geochemical composition and therefore identified by its geographic origin. Based on these data, the elements useful as possible geochemical fingerprints for “Prosecco” wine are, in order of relevance, B, Ca, Mo, Sb and Sr.

Conclusions

Major and trace elements in soil and wine samples from four vineyards of the Veneto Region (Northern Italy) were evaluated as possible geographical markers useful to establish geochemical fingerprints of the renowned Controlled Designation of Origin (DOC) “Prosecco” wine. The geochemical analyses of soil samples by ICP-MS characterized a set of major and trace elements specific for the geographical origin of each vineyard. The box plots based on ICP-MS data showed that the distribution of major and trace elements in soil samples matched that of wine samples from the same location. The distribution of major and trace elements in wine samples was apparently linked not only to winemaking processes but also to geographical origin.

The LDA multivariate analysis confirmed that the elements showing geochemical correlations in all locations were B, Ca, Mo, Sb and Sr. Among them, the most suitable to establish a reliable correlation between geolithological features of soil and chemical composition of wine were B and Sr. Based on these results, it was possible to discriminate the vineyard soils according to geo-lithological characteristics of each area. These elements therefore represent geochemical fingerprints of the “Prosecco” wine and could be useful to prevent falsification and fraudulent use of wine label.

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Figure Captions

Fig. 1 Geological map of the Veneto Region (Italy) showing the location of the four vineyards studied: (1) Bagnoli di Sopra, (2) Braga, (3) Broscagin, (4) Peraro.

Fig. 2 Bivariate plots of abundances of Al versus Rb (a), Fe versus V (b), and Cr versus Ni (c) determined by inductively coupled plasma mass spectrometry (ICP-MS) in soil samples from the four vineyards. Values of elements are expressed in mg/kg.

Fig. 3 Box Plots of the major elements Al (a), Ca (b), Mg (c) and Na (d) determined by ICP-MS in soils from the four vineyards. Values of major elements are expressed in mg/kg.

Fig. 4 Box Plots of the trace elements As (a), Ba (b), B (c), Cu (d), Cr (e), Ni (f), Pb (g), Rb (h) and Sn (i) determined by ICP-MS in soils from the four vineyards. Values of trace elements are expressed in mg/kg.

Fig. 5 Box Plots of the major elements Ca (a), K (b) Mg (c) and Na (d) determined by ICP-MS in wine samples from the four vineyards. Values of major elements are expressed in mg/kg.

Fig. 6 Box Plots of the trace elements B (a), Cu (b), Li (c), Mn (d), Pb (e), Rb (f) Sn (g), Sr (h) and Ti (i) determined by ICP-MS in wine samples from the four vineyards. Values of B, Cu, Mn, Rb, Sr and Ti are expressed in mg/kg and values of Li, Pb and Sn are expressed in µg/kg.

Fig. 7 Linear regression values of concentrations of Sr versus B in soil (a) and wine samples (b) of the four vineyards, showing a significant correlation ($R^2 > 0.60$) with an internal and external 95% confidence interval. Values of trace elements are expressed in mg/kg.

Fig. 8 Linear discriminant analysis (LDA) plots of the concentrations of all elements in soil (a) and wine samples (b) from the four vineyards.

Table 1 Concentrations of elements in soil samples from the four vineyards, analyzed by inductively coupled plasma mass spectrometry (ICP-MS). A non-parametric multiple test (Test di Kruskal-Wallis) was applied. P-values: ns= not significant; *< 0.05; ** < 0.01; *** < 0.001. Values are expressed in mg/kg.

Table 2 Concentrations of elements in wine samples from the four vineyards, analyzed by ICP-MS. Values are expressed in mg/kg from Al to Zn and in µg/kg from As to V. All abbreviations as in Table 1.

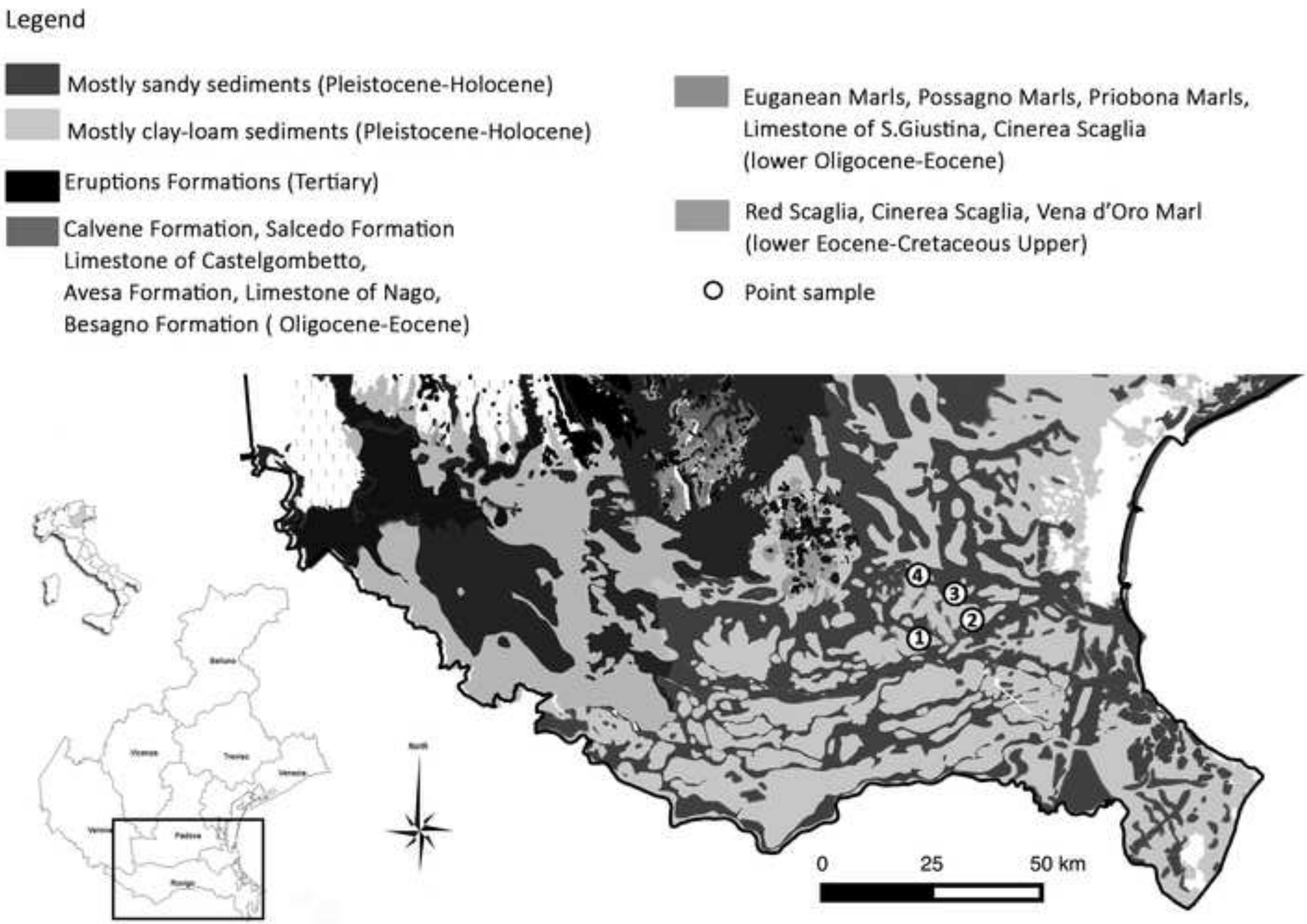

Legend
Mostly sandy sediments (Pleistocene-Holocene)
Mostly clay-loam sediments (Pleistocene-Holocene)
Eruptions Formations (Tertiary)
Calvene Formation, Salcedo Formation
Limestone of Castelgombetto,
Avesa Formation, Limestone of Nago,
Besagno Formation (Oligocene-Eocene)
Euganean Marls, Possagno Marls, Priobona Marls,
Limestone of S.Giustina, Cinerea Scaglia
(lower Oligocene-Eocene)
Red Scaglia, Cinerea Scaglia, Vena d'Oro Marl
(lower Eocene-Cretaceous Upper)
Point sample
1
2
3
4
0
25
50 km

Figure2

Click here to download Figure Fig.2_Pepi_and_Vaccaro.tif

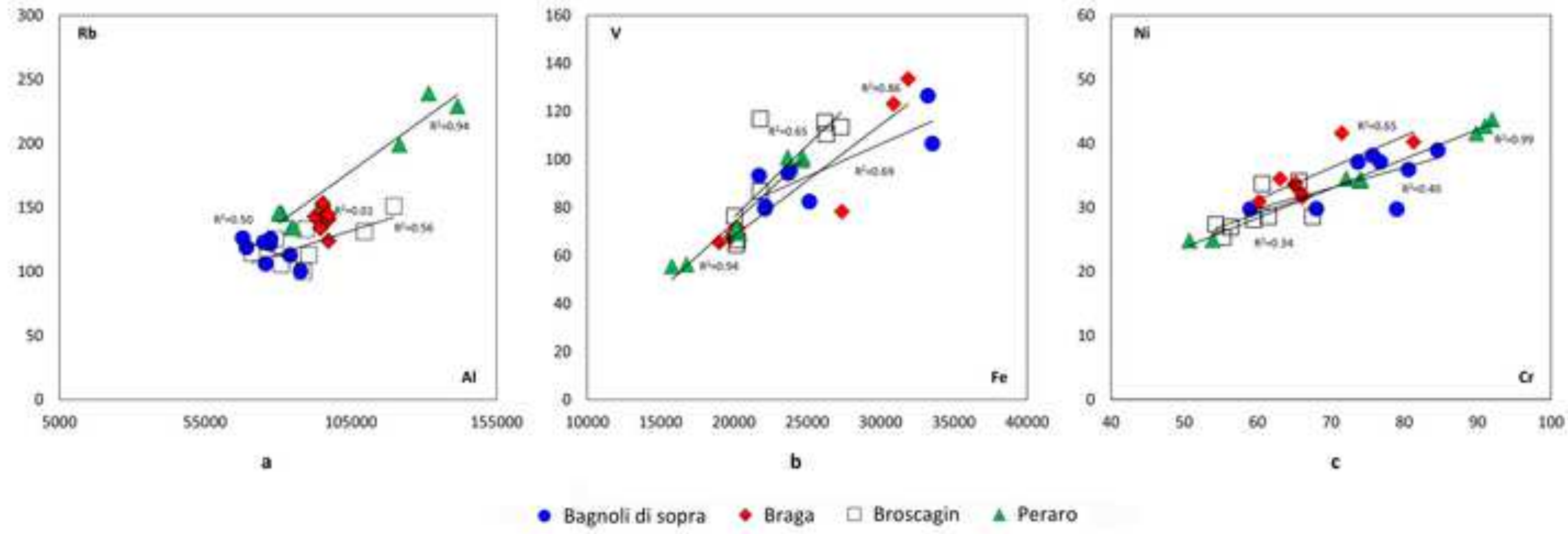


Figure3

Click here to download Figure Fig.3_Pepi_and_Vaccaro.tif

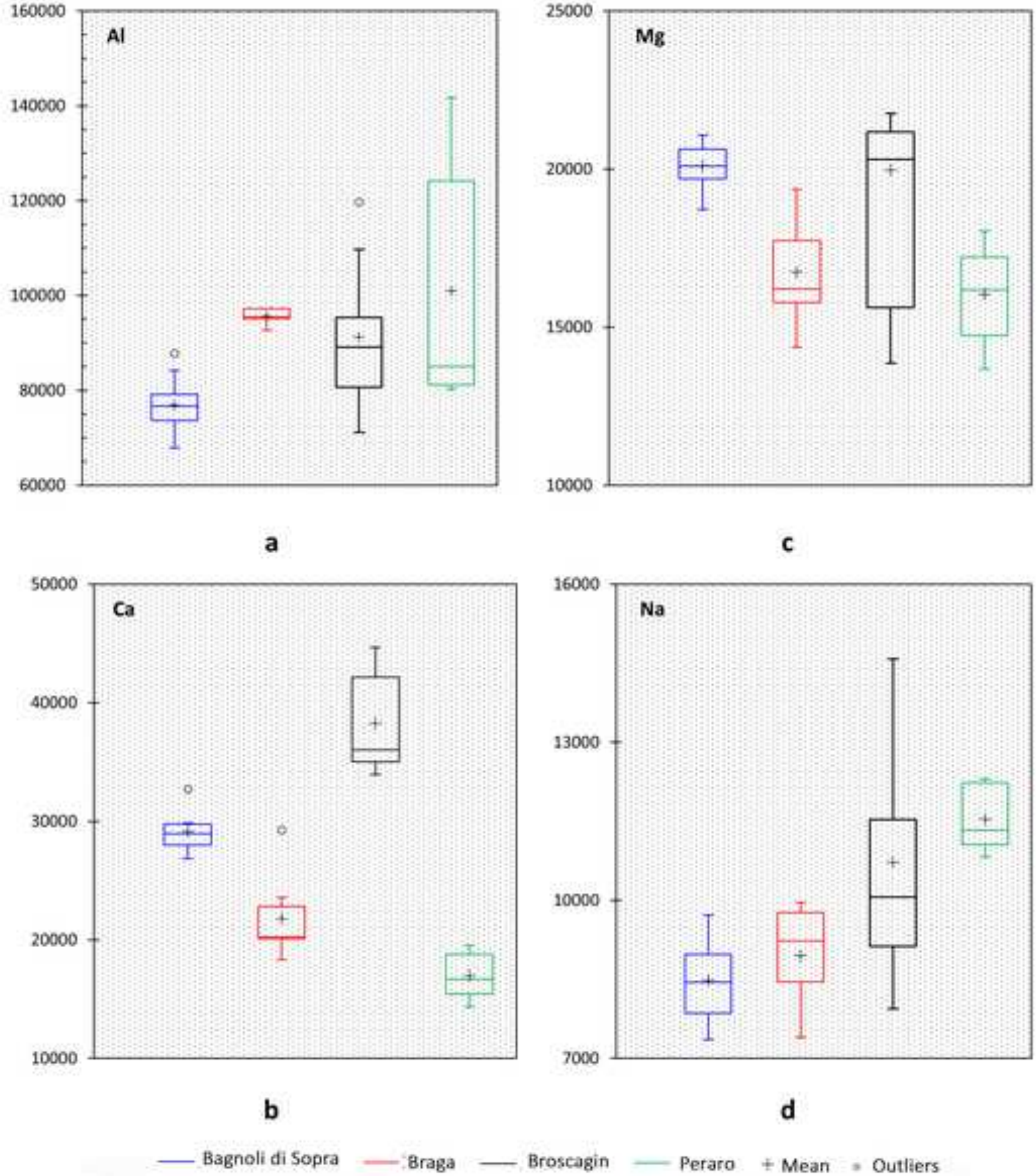
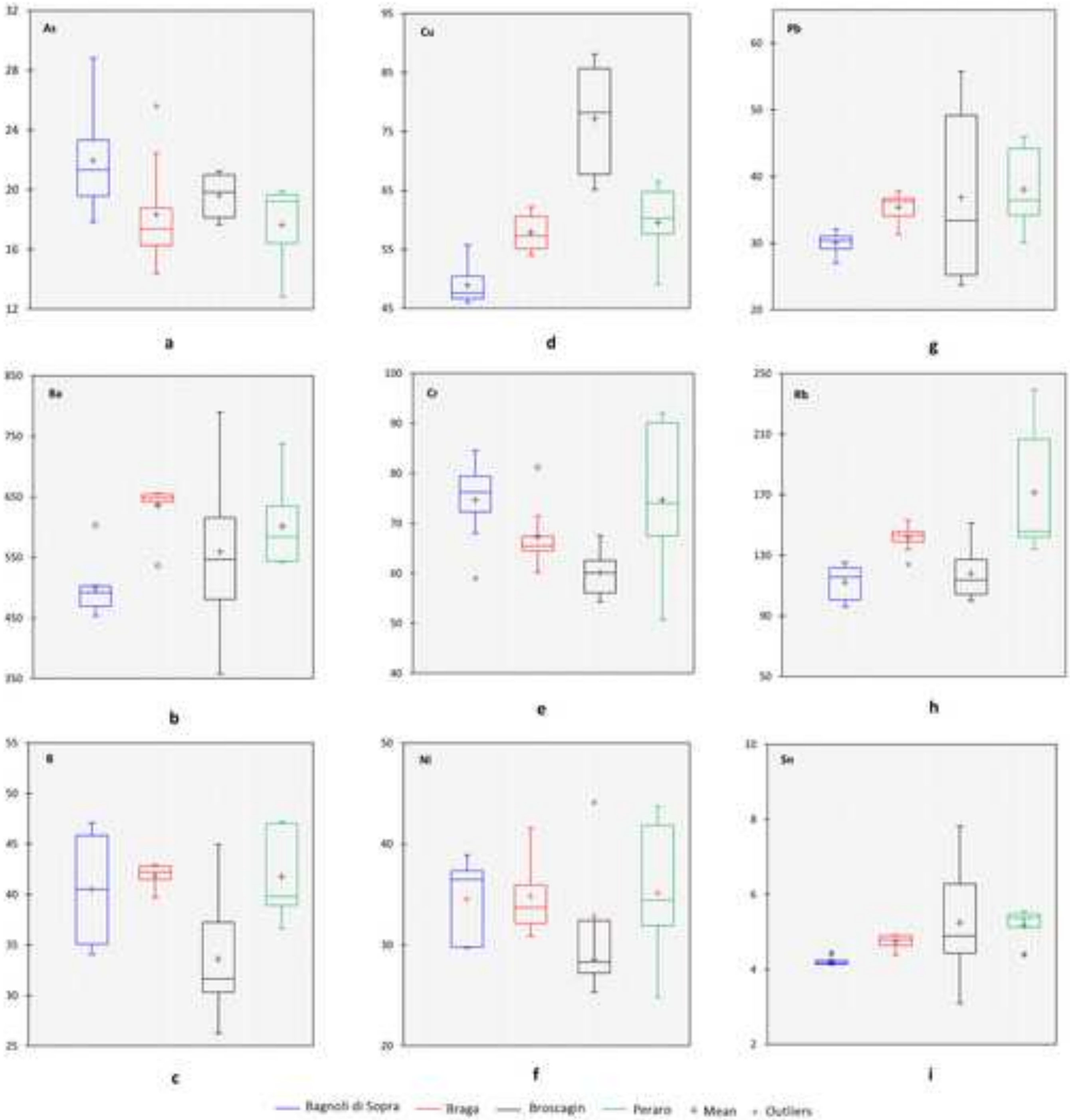


Figure4

Click here to download Figure Fig.4_Pepi_and_Vaccaro.tif



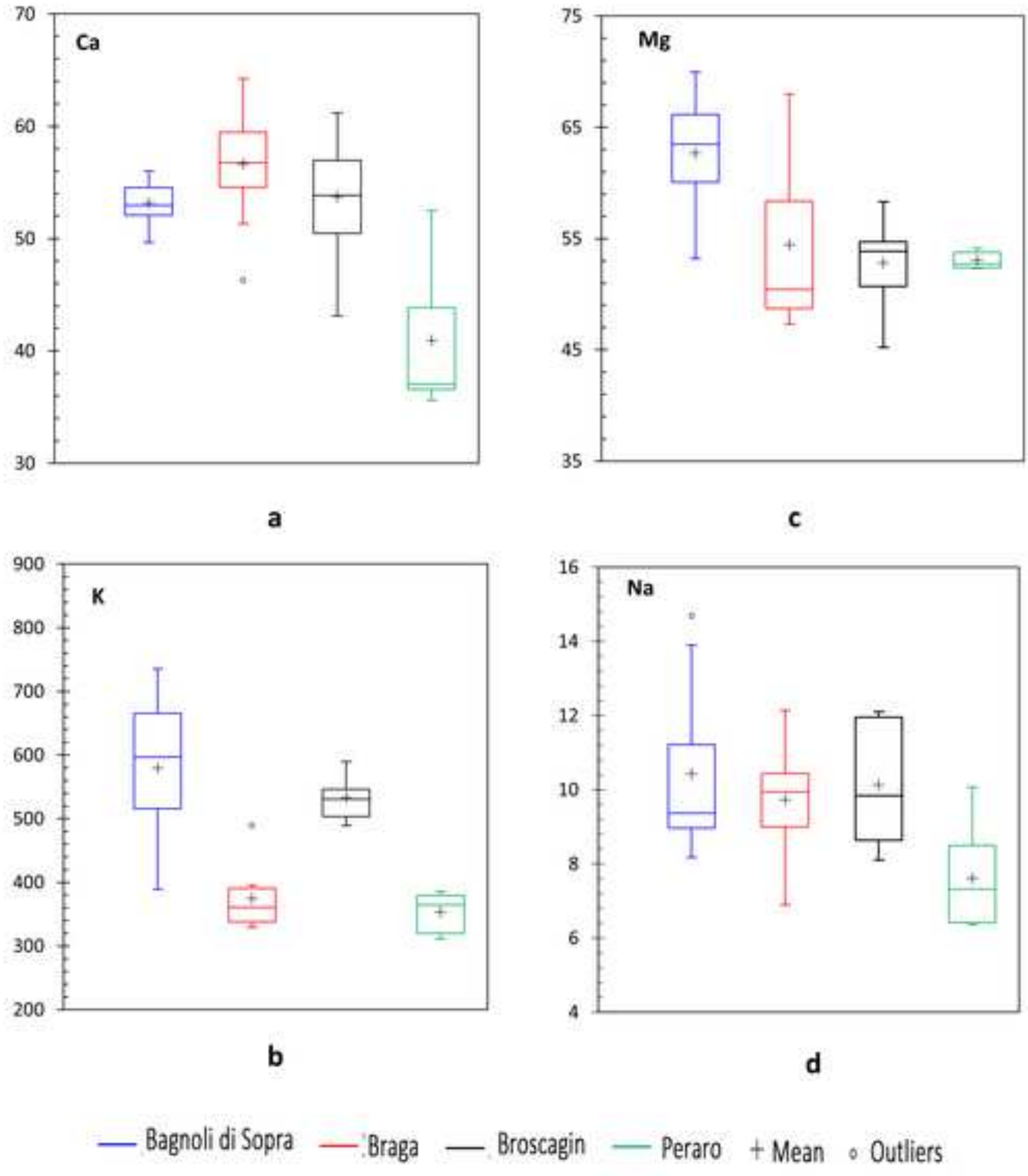
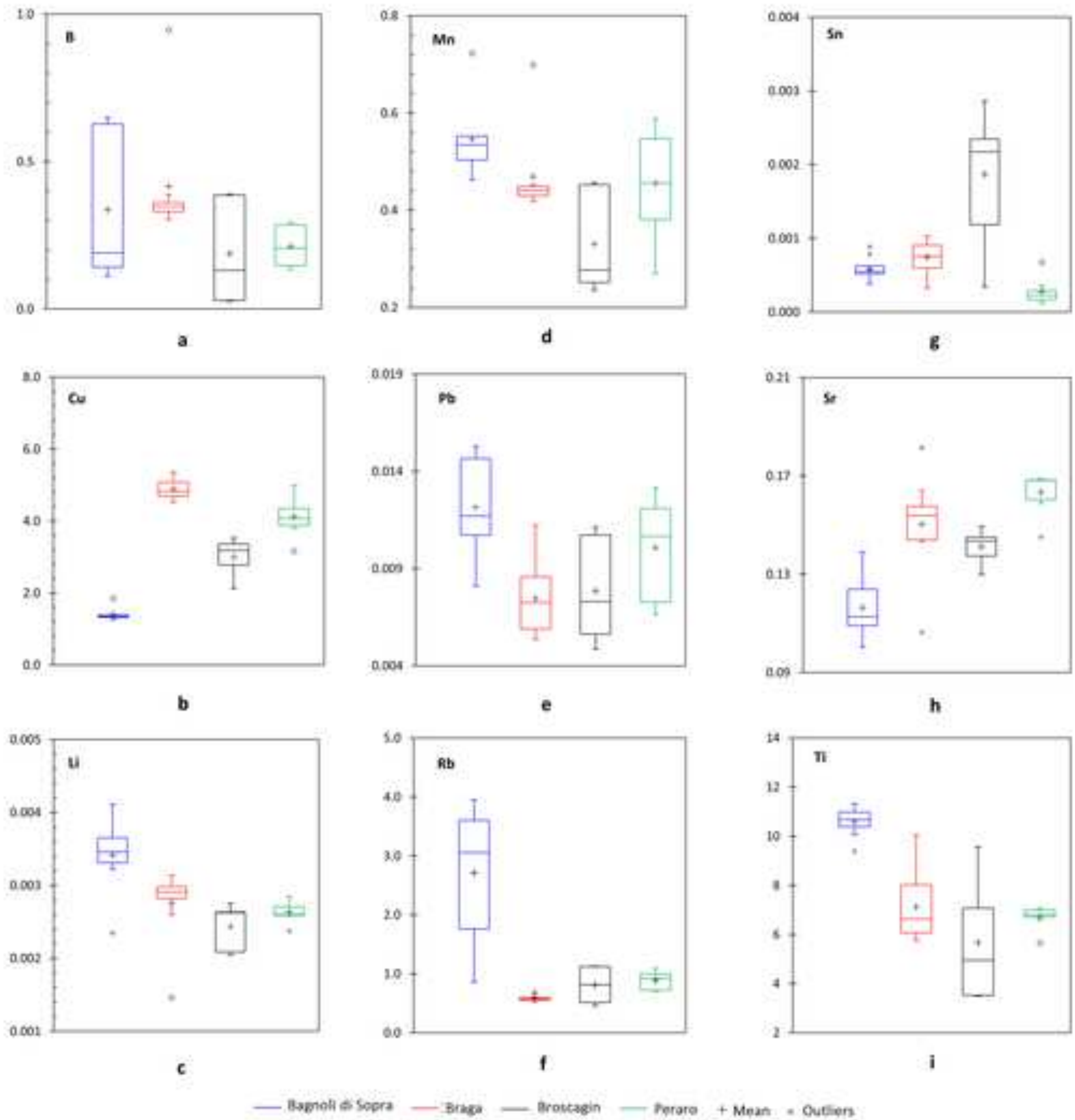

Ca
70
60
50
40
30
a
Mg
75
65
55
45
35
c
K
900
800
700
600
500
400
300
200
b
Na
16
14
12
10
8
6
4
d
Bagnoli di Sopra
Braga
Broscagin
Peraro
Mean
Outliers

Figure6


B
Mn
Sn
Cu
Pb
Sr
Li
Rb
Ti
a
d
g
b
e
h
c
f
i
Bagnoli di Sopra
Braga
Broscagin
Peraro
Mean
Outliers

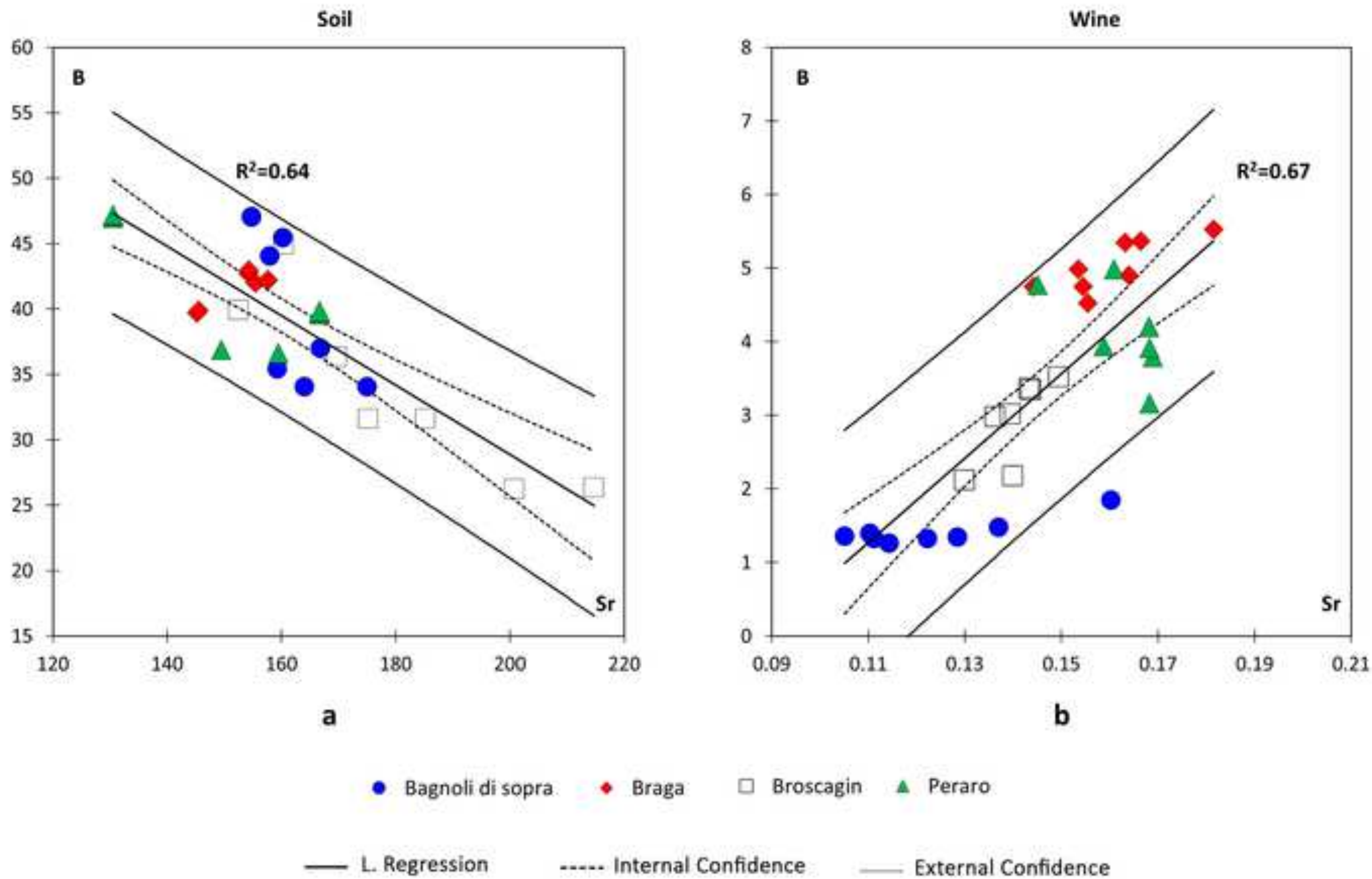
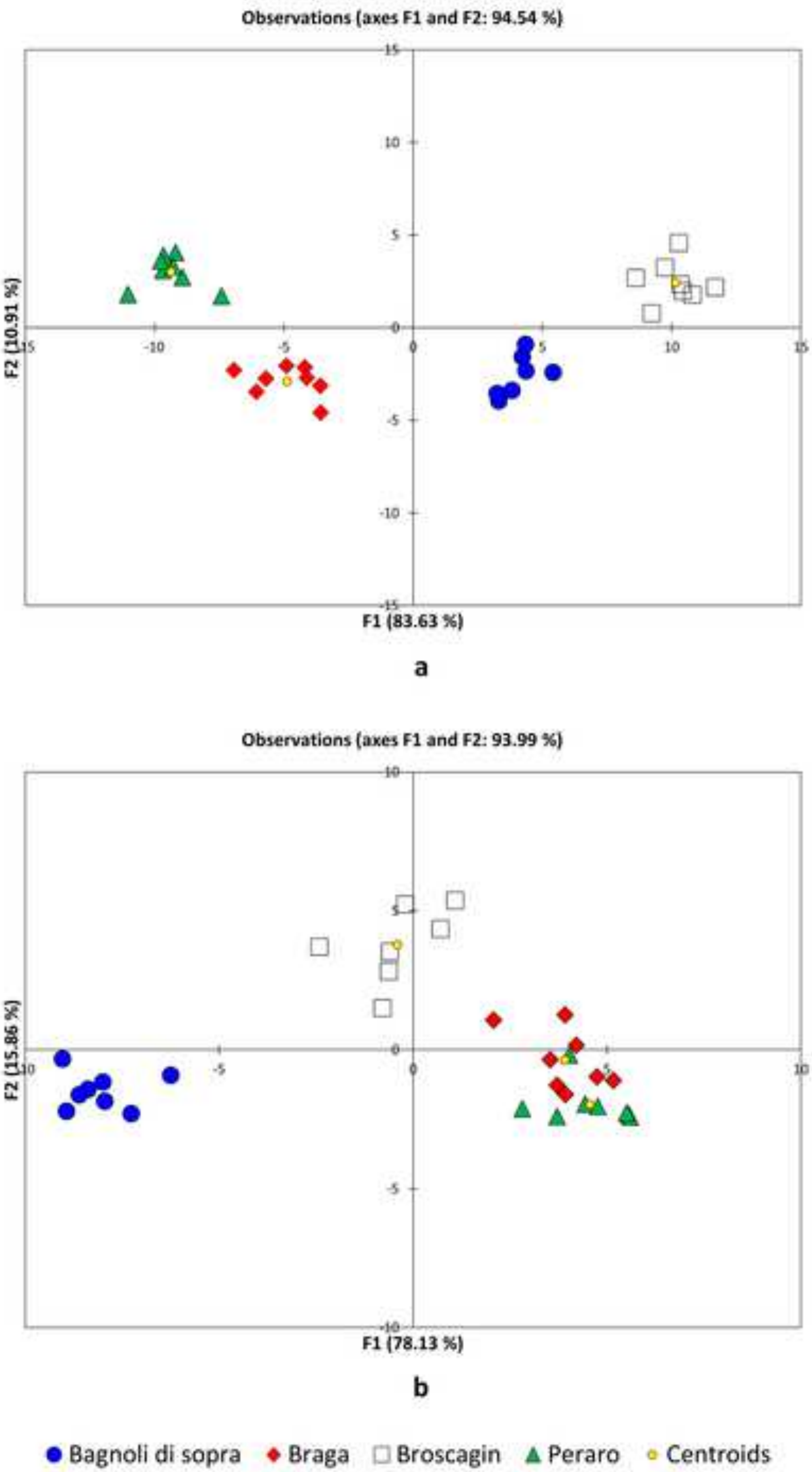

Soil
Wine
B
R^2=0.64
R^2=0.67
Sr
60
55
50
45
40
35
30
25
20
15
120
140
160
180
200
220
8
7
6
5
4
3
2
1
0
0.09
0.11
0.13
0.15
0.17
0.19
0.21
a
b
Bagnoli di sopra
Braga
Broscagin
Peraro
L. Regression
Internal Confidence
External Confidence

Figure8 Click here to download Figure Fig.8_Pepi_and_Vaccaro.tif



	Bagnoli di Sopra	Braga	Broscagin	Peraro	p-value
Al	76618.92±6740.60	95473.13±1615.3	89102.65±16096.9	85043.51±26063.0	***
As	21.33±3.56	17.38±3.8	19.84±1.49	19.21±3.05	*
B	40.53±5.89	42.23±1.30	31.64±6.48	39.80±4.61	*
Ba	492.10±46.9	648.37±40.2	546.64±136.10	583.88±70.6	***
Ca	28967.51±1771.4	20234.13±3443.8	35998.82±4345.8	16703.65±2081.5	***
Co	15.37±1.43	16.14±1.20	14.10±5.16	15.15±1.85	n.s
Cr	76.24±8.0	65.53±6.5	60.10±4.8	74.00±16.1	*
Cu	47.60±3.4	57.31±3.3	78.20±9.42	60.28±6.61	***
Fe	23787.04±4887.01	20228.87±5442.7	21800.07±3091.12	20332.19±3391.0	*
K	21101.58±4173.3	18685.51±2166.7	19710.93±8525.78	24102.81±5677.6	n.s
Li	66.15±7.8	80.97±5.60	60.53±11.07	72.39±5.31	***
Mg	20088.21±769.2	16204.78±1692.5	20303.50±5639.2	16173.69±1577.03	**
Mn	640.21±66.45	581.79±34.2	638.15±192.47	804.12±56.7	***
Mo	0.86±0.17	1.13±0.10	0.67±0.24	0.84±0.15	**
Na	8442.65±870.5	9233.00±1054.7	10066.01±2460.1	11335.90±644.5	***
Ni	36.48±4.06	33.70±3.4	28.31±10.31	34.45±7.41	*
Pb	30.42±1.6	36.25±2.10	33.40±12.9	36.43±6.22	**
Rb	115.75±11.7	143.22±9.25	113.67±17.6	145.76±40.90	***
Sb	1.18±0.06	1.51±0.13	1.08±0.42	1.49±0.15	***
Se	1.00±0.30	1.05±0.4	1.36±0.32	1.02±0.26	n.s
Sn	4.17±0.13	4.79±0.20	4.89±1.6	5.38±0.50	***
Sr	159.75±7.08	154.31±5.10	175.21±20.5	154.45±16.7	***
Ti	3663.11±825.7	4184.04±962.5	4139.83±756.8	3554.39±376.8	n.s
Tl	0.87±0.22	2.32±0.73	1.31±0.21	1.04±0.53	n.s
V	93.72±10.48	70.7±27.5	98.61±22.8	71.10±19.54	*
Zn	97.67±5.59	118.98±12.40	106.88±35.2	106.96±15.40	n.s

Table2 Click here to download Table Table.2_Pepi_and_Vaccaro.docx

	Bagnoli di Sopra	Braga	Broscagin	Peraro	p-value
Al	0.33±0.11	0.38±0.03	0.32±0.03	0.30±0.02	**
B	1.35±0.18	4.94±0.33	3.81±0.55	4.07±0.47	***
Ca	52.98±2.12	56.75±6.05	53.83±6.03	37.04±5.76	*
Cu	0.19±0.05	0.35±0.12	0.13±0.08	0.21±0.08	*
Fe	0.53±0.11	0.36±0.16	0.45±0.08	0.36±0.09	n.s
K	597.14±129.7	361.17±33.7	531.01±27.13	364.70±32.50	***
Mg	63.47±6.04	50.44±8.70	53.85±3.07	52.73±0.81	**
Mn	0.53±0.08	0.44±0.09	0.28±0.10	0.46±0.02	***
Na	9.37±2.49	9.95±1.51	9.84±1.67	7.32±1.38	n.s
Rb	3.06±1.18	0.58±0.06	0.82±0.33	0.92±0.15	n.s
Sr	0.11±0.01	0.15±0.02	0.14±0.01	0.17±0.01	**
Ti	10.68±0.62	6.63±1.50	4.95±1.42	6.81±0.46	n.s
Zn	0.41±0.19	0.26±0.14	0.63±0.14	0.62±0.15	n.s
As	15.63±2.04	18.94±4.0	14.82±3.86	12.17±3.20	*
Ba	45.87±11.7	43.46±9.96	46.54±4.25	56.63±7.04	n.s
Co	2.31±0.27	2.13±0.38	3.20±0.98	2.05±0.89	n.s
Cr	29.31±11.33	5.33±2.82	5.36±20.7	20.31±1.14	n.s
Li	2.96±0.52	2.41±0.55	2.12±0.30	2.11±0.16	***
Mo	1.43±0.21	0.29±0.08	1.51±0.57	0.07±0.04	***
Ni	32.11±6.37	24.78±4.78	16.42±4.57	18.45±5.87	***
Pb	11.71±2.56	7.25±2.08	7.30±1.66	10.66±2.68	***
Se	96.96±33.56	46.26±8.05	46.31±4.15	7.49±1.83	n.s
Sb	0.50±0.35	0.43±0.07	0.33±0.10	0.32±0.05	n.s
Sn	0.55±0.17	0.76±0.24	2.17±0.78	0.23±0.08	n.s
Tl	0.41±0.24	0.17±0.09	0.18±0.05	0.24±0.06	*
V	1.86±0.56	1.50±0.48	1.47±0.21	1.44±0.08	**