Geochemical influence of soil on leaf and grape (*Vitis vinifera* L. ‘Cencibel’) composition in La Mancha region (Spain)

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**Summary**

The main purpose of the study was to evaluate major and trace elements contained in topsoil from representative plots of vineyards located in La Mancha, Spain, to obtain an elemental fingerprint of vines.

The samples evaluated were obtained from topsoil in six different plots, belonging to the region of La Mancha, characterized by the cultivation of vineyards (near 189.127 ha). Twenty different vines from each plot were chosen to take samples from grapes, petioles and leaves. Analyses were carried out by X-ray Fluorescence applied on soils and dried vegetal matter. Biological Absorption Coefficient (BAC) was calculated to assess the uptake of minerals by vines as a function of their specific content in soil.

The BAC in leaves and grapes was very similar for all studied elements. High contents of Ca, Sr, Ni and rare earth elements (La, Ce and Nd) were found along with low contents in Al, Zr, Ba, Cu, Zn and Pb, and normal contents in the rest of the elements.

BAC in grapes was lower for the majority of the studied elements but it is interesting to underline the contents of Cs, K, Nb, Ce, Zn and Sr as possible markers of soil fingerprinting in the resulting wines.

**Key words:** Trace elements, Strontium, vine physiology.

**Introduction**

The chemical interaction between soil-plant systems is characterized by the contents of the different elements. In this sense, each particular system has its own specific constituents. The elemental composition in wines and grapes has been extensively studied in order to evaluate the characteristics associated with the different regions and varieties, mainly in an attempt to obtain an elemental fingerprint for products to certify designations of origin. In general, the vineyards cultivated in the region of La Mancha produce wines with their own designation of origin (D.O. La Mancha). This region represents the world’s largest vineyard area, with 189,127 ha, and it is formed by four provinces, Toledo, Albacete, Cuenca and Ciudad Real (HIDALGO 1980). Evaluation of the geochemical properties of the vines and comparison of the elemental contents in soils could be of great interest for the region. For example, it would be possible to assess the influence of other factors on the composition of wines along with the soil plant interactions in major and trace elements, and to detect any external variation in the elemental contents, mainly as a consequence of diffuse pollution. The soils in the aforementioned area originate from Tertiary sediments (Miocene) (HIDALGO 1980). These soils were formed over Ordovician-Silurian rocks and originate from the erosion and weathering of the old Hercinic socket. In general, the soils of the region are classified as Luvisols, with rhodic or chronic character, due to the presence of iron oxides (FAO ISRIC ISSS, 2006). The main materials found over the Hercinic socket result from the weathering and erosion of quartzite and materials from the schist-greywacke complex. However, the soils from the region of Ciudad Real have not been studied in great detail.

The different properties of wine cultivars are greatly influenced by soil characteristics, chiefly texture and content of macro and micronutrients. Several studies have been carried out on Mediterranean regions and areas of influence to investigate soil origins, parent materials and their characteristics (CARLEVALIS et al. 1992, ATALAY 1997, GARCÍA and SANTOS 1997, YAALON 1997, YASSOGLOU et al. 1997, ORTIZ et al. 2002, BRONGER and SEDOV 2003). Indeed, recently published studies have focussed on the area under consideration in this paper (DE LA HORRA et al. 2008, CONDE et al. 2009).

The study of geochemical soil composition provides information, along with other complementary data, about fertility and the availability of nutrients for plants. Major elements provide information about total structural components and potential nutrients (WILD 1992, LANYON et al. 2004, WHITE 2009), while contents of trace elements give an insight into the geochemical origin (GARCÍA et al. 2009) and potential toxicities (CONDE et al. 2009) of the soil.

The metabolism of trace elements in plants has been widely studied (WILD 1992, KABATA-PENDIAS 2001). However, every plant-soil system (KABATA-PENDIAS 2001, MOLINA et al. 2006) has to be specifically studied, since the behaviour could differ depending on the elements present in a particular system. In all cases studied previously, plant composition (leaves, fruits, juices, tubers, etc.) always reflected the chemical properties from the environment of...
Given the importance of the aspects outlined above, the main objective of the work described here was to characterize the contents of major and trace elements in different parts of the vines from the region of Campo de Calatrava, the varied soils and vineyards of which are representative of La Mancha Region (Ciudad Real, Spain). Another aim was to assess the pattern in the accumulation of major and trace elements in the different parts of the vines.

Materials and Methods

Studied area: The area under investigation was near to the municipality of Carrión de Calatrava in the province of Ciudad Real (Fig. 1). This location was chosen because of its soil diversity and because the vineyards cultivated are of the ‘Cencibel’ variety (‘Tempranillo’) grafted onto ‘110-Richter’. Dry farming and low vine conduction, pruned in spurs is the traditional management regime in this area (the La Mancha Region has its own designation of origin, D.O. La Mancha). These soils represent 27.2% of the total regional area dedicated to the cultivation of the wine grape (Hidalgo 1980, Amorós et al. 2008). The main use of the cultivars is in the production of premium-quality wines (Pillet 2007).

The area is formed by a smooth topography with alternating quartzitic hills (Amorós et al. 2010) and Miocene plains. The valleys show hydromorphic soils and quaternary sediments. In addition, some volcanic intrusions could be present within the described elements. The great variability of soils with different geological origins and specific evolutions offers one of the greatest edaphically diverse regions of the World (De la Horra et al. 2008, Carlevalis et al. 1992).

The altitude and locations of the plots are indicated in Tab. 1. The samples evaluated were obtained from topsoil in six different plots, with three samples taken from
Properties of plots. Altitude, location, organic matter, active lime and total carbonates

| Plot identification | Altitude (m) | Coordinates | Organic matter (%) | Active lime (%) | % CaCO$_3$
|---------------------|-------------|-------------|--------------------|----------------|--------
| M1                  | 623         | 39º05'09.1'' – 03º51'09.1'' | 1.9               | 2.50           | 4.5    
| M2                  | 627         | 39º03'31.9'' – 03º49'00.6'' | 1.5               | 7.38           | 16.4  
| M3                  | 636         | 39º02'41.1'' – 03º52'12.3'' | 1.2               | 10.63          | 9.8   
| M4                  | 621         | 39º03'23.3'' – 03º52'31.9'' | 3.2               | 10.63          | 23.9  
| M5                  | 618         | 39º03'11.7'' – 03º52'36.2'' | 1.0               | 3.00           | 3.0   
| M6                  | 631         | 39º02'08.7'' – 03º52'33.0'' | 3.6               | 14.88          | 25.5  

Geological influence of soil in La Mancha

Table 1

| Plot identification | Altitude (m) | Coordinates | Organic matter (%) | Active lime (%) | % CaCO$_3$
|---------------------|-------------|-------------|--------------------|----------------|--------
| M1                  | 623         | 39º05'09.1'' – 03º51'09.1'' | 1.9               | 2.50           | 4.5    
| M2                  | 627         | 39º03'31.9'' – 03º49'00.6'' | 1.5               | 7.38           | 16.4  
| M3                  | 636         | 39º02'41.1'' – 03º52'12.3'' | 1.2               | 10.63          | 9.8   
| M4                  | 621         | 39º03'23.3'' – 03º52'31.9'' | 3.2               | 10.63          | 23.9  
| M5                  | 618         | 39º03'11.7'' – 03º52'36.2'' | 1.0               | 3.00           | 3.0   
| M6                  | 631         | 39º02'08.7'' – 03º52'33.0'' | 3.6               | 14.88          | 25.5  

The software packages Microsoft Office EXCEL 2007 (Copyright© Microsoft 2008) and STATGRAPHICS Plus 5.1 (Copyright© 1994-2000 Statistical Graphics Corp.) were used for statistical analyses and to produce figures.

Results and Discussion

Soil characteristics: General data for the soils of the studied plots are given in Tabs 1 and 2. Even soils located in plots next to each other show large variation in their properties. In particular, the organic matter content is highly variable due to the different manure systems used by each farmer. These soils have a basic pH and they contain medium to high contents of calcium carbonate. These soil characteristics are very common in the region of La Mancha (Carlevalis et al. 1992, Hidalgo 1980, De la Horra et al. 2008). In this particular case, the mobilization of metallic elements that are normally adsorbed in clay (Kabata-Pendias 2001) is more effective in acidic media (Wild 1992, White 2009). The electrical conductivity results do not suggest any problem related to salinity (Wild 1992). The most frequent textural class is the loam type, with a clay content that does not exceed 20%.

Soils were classified as Chromic Luvisols or Petric Calcisolos (FAO ISRIC ISSS, 2006). A description of the soils has been published previously (De la Horra et al. 2008, Carlevalis et al. 1992, Amorós et al. 2010).

Contents of major elements in the soil-plant system: The results for the total contents of major and trace elements are shown in Tab. 3 for each plot. The data are arranged from 1 to 6, according to the number of plot. The first six results are denoted CE and these represent the soils. The CE designation comes from the name of the vine variety cultivated in the studied plots, which is known as 'Cencibel' in La Mancha ('Tempranillo') is the best-known name worldwide since it is used in La
Major and trace elements in soils, leaves and fruits. The identification starts with the number of the plot, from 1 to 6, to show which sample belongs to each plot. CE is the identification for the soil samples, CEH for the leaf samples, CEP for petiole samples and CEU for grape samples. The concentrations are expressed in % for major elements (from Na to K) and in ppm for trace elements (from V to Nd). All results are given on the basis of dry matter.

The results obtained on the soil range from 15 to 20 ppm. How treatments are not frequent and this element does not reach the region (0.82 %), mainly when the results are compared with those for soils from granitic regions (HUGGET 2006). The Ca/Mg and Ca/K ratios are high and they can result in absorption problems for Mg and K (LANYON et al. 2004).

However, the most frequent problem is ferric chlorosis due to low Fe absorption, which can decrease the productivity even without any evident symptoms (GRUBER 2002).

Mn contents are low when presented as an average value (0.065 %) with the exception of plot 4, which contains remnants of volcanic rocks. A high Mn content has been pointed out as being responsible for the particular nature of some wines from Beaujolais (HUGGET 2006).

Contents of trace elements in the soil-vine system: The presence of low levels of Zn (41 ppm) and Pb (19 ppm) is inferior as compared to other wine-growing regions such as Champagne (300 ppm and 100 ppm, respectively) (CHOPIN et al. 2008), Oporto (ALMEIDA and VASCONCELOS 2003) and other areas that have suffered contamination by spills (MADEJON et al. 2003).

Data for Cu were not included in Tabs 3 and 4 because results obtained on the soil range from 15 to 20 ppm. However, variations in the Cu content for leaves range from below the limit of detection to 133 ppm, depending on whether the plot has recently undergone fungicidal treatment or not. Significant amounts of Cu were detected when the plots showed symptoms of contamination through treatment (POHL 2007). In any case, in the studied area, Cu treatments are not frequent and this element does not reach the levels found in other wine-growing regions, which have typical values of around 100 ppm (ALMEIDA and VASCONCELOS 2003, CHOPIN et al. 2008).

The particularly high Fe levels found in these soils warrant special mention, even if this element is present in normal proportions (3.8 %) with respect to world soils (WILD 1992) and other soils of La Mancha (CARLEVALIS et al. 1992, DE LA Horra et al. 2008). However, some symptoms of chlorosis were apparent due to the presence of Ca and the high pH of the soil solution (GRUBER 2002), a problem that can be especially prevalent if the rootstock

### Table 3

<table>
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<tr>
<th>Plot</th>
<th>Na</th>
<th>Mg</th>
<th>Al</th>
<th>Si</th>
<th>K</th>
<th>Ca</th>
<th>Mn</th>
<th>Fe</th>
<th>Ni</th>
<th>Cu</th>
<th>Zn</th>
<th>Pb</th>
<th>Cr</th>
<th>Mo</th>
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<td>3.0</td>
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<td>0.3</td>
<td>0.2</td>
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<td>0.05</td>
<td>0.01</td>
<td>0.005</td>
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<td>0.3</td>
<td>0.2</td>
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<td>0.05</td>
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<td>0.005</td>
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Table 4

Average (X) and standard deviation (S) for major and trace elements. For identification purposes, s is used for soil, h for leaf, p for petiole and u for grape samples. The concentrations are expressed in % for major elements (from Na to K) and in ppm for trace elements (from V to Nd). Biosorption levels are represented by Biological Absorption Coefficient (BAC) followed by H for leaf, P for petiole and U for grape

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<th>Xh</th>
<th>Sh</th>
<th>Xp</th>
<th>Sp</th>
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<th>Su</th>
<th>BACH</th>
<th>BACP</th>
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<td>0.026</td>
<td>0.007</td>
<td>0.006</td>
<td>0.025</td>
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<td>0.010</td>
<td>0.009</td>
<td>0.089</td>
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<td>Mg</td>
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<td>0.130</td>
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<td>0.103</td>
<td>0.619</td>
<td>0.146</td>
<td>0.039</td>
<td>0.014</td>
<td>0.480</td>
<td>0.672</td>
<td>0.043</td>
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<td>0.011</td>
<td>0.007</td>
<td>0.002</td>
<td>0.004</td>
<td>0.005</td>
<td>0.014</td>
<td>0.002</td>
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<td>0.008</td>
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<td>0.072</td>
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</tbody>
</table>

is not chosen appropriately (Wooldridge 2010). The Ba/Sr ratio is displaced due to the abundance of Sr in the lime-stone soils of La Mancha (Conde et al. 2009) and because the content of Ba is low compared with the average for world soils (Kabata-Pendias 2001). Sr is of special interest because it can replace the Ca in many physiological and structural features due to the similar ionic radius of these elements (Rollingsson 1993).

The abundance of Ni is relatively high, at 43 ppm, without reaching levels of contamination (Reinmann 2001).

Rare earth elements (REE) are also present and particularly abundant are Ce (64 ppm) and Nd (29 ppm). The La content is around 30 ppm, showing low levels of amount in the plant and, for that reason data were not shown in Tab. 3. Other trace elements such as V, Cr and Co are at normal or low levels. The content of Rb is particularly low. This element is characteristic of granitic areas (Almeida and Vasconcelos 2003, Hugget 2006). The behaviour of Rb is of interest as it can replace the K in physiological functions as these elements have a similar ionic radius (Rollingsson 1993).

In relation to the content of trace elements in the plant, it can be stated that there are very few global references, although major elements and micronutrients have been widely studied (Lanyon et al. 2004, White 2009). The contents of the different elements found in vines of the studied region, when compared to other plants referred in the bibliography (Kabata-Pendias 2001), can be summarized as follows:

- Similar contents: Ca, K, Mg, Ba, Cu, Mn and Ni
- Higher contents: P, S, Co, Cr and V
- Lower contents: Na, Pb and Zn.

It can be observed from the results in Tab. 3 that certain elements accumulate in the plant, e.g. Cs (Kabata-Pendias 2001). The role of fungi in the uptake of nutrients (White, 2009) has been pointed out for elements such as P (Kabata-Pendias 2001, White 2009) in the active participation of the absorption and mobilization of trace elements (Campos et al. 2009). This pattern was not found in our case for Rb (low content in the studied soils) or Cd (not detected by the analytical technique used). We agree in pointing out elements that are very weakly uptaken as Zr, Sc, Fe and Al (Kabata-Pendias 2001). However, the Ba content showed a relatively high level in our plots.

Regarding the published foliar analysis data for evaluating the nutritional status of the vine (Wild 1992, 2009 Lanyon et al. 2004), all elements obtained in our study are within the limits that are considered normal, with the exceptions of K (0.7 %) and Zn (15 ppm), which are present at relatively low levels without reaching deficiency. In other regions, such as the Douro in Portugal (Pessanha et al. 2010), similar results for leaves were obtained in K, Ca and Fe, higher levels in Cu, Zn and Rb and lower levels in Sr. In the Champagne region, Chopin et al. (2008) twice the amount of Zn in leaves and very similar contents for Pb in comparison to our study.

The contents of different elements in leaves and petioles are shown in Tab. 3 and it can be observed that the
contents are similar for the trace elements. The major elements do show some differences, for example in Na, where the content is higher in petiole, and in Al, Si, Ca, S, Ca, Mn and Fe, which show lower values in petioles than in leaves. Several differences could also be detected in some major elements (P, K, Ca and Mg) depending on the variety and rootstock (Wooldridge 2010).

According to the results in Tab. 3, the contents for the different elements in the fruit are always lower than in the leaves, except for K, since the accumulation of this element is reported to increase as the fruit ages (White 2009).

On the other hand, the contents of some trace elements could enable differentiation of the origin of products, in keeping with other trace and major elements described in the bibliography that could be of interest in relating the plant with the soil of provenance (Ba, Cr, Li, Rb, Sr, Ca, Mg, Mn and Na) (Casanás et al. 2003, Kmendt et al. 2005, Pohl 2007, Di Giacomo et al. 2007, Almeida and Vasconcelos 2003, Galgano et al. 2008).

In the Douro region (Portugal), Pessanha et al. (2010) obtained similar results in cultivars for K, Fe and Zn, higher levels for Cu and Rb and lower levels for Ca and Sr. The contents obtained for trace elements are very low in comparison to other regions and species, particularly if the soil suffered some contamination (Reinmann 2001, Madejon 2003).

Bioaccumulation of elements: The level of bioaccumulation was calculated as the ratio between the concentration of any studied element in the leaf, petiole or grape of the vine and the concentration found in the corresponding soil. The capacity of a plant to uptake nutrients is measured as the ratio of the element in the plant and its concentration in the soil. This ratio is called the Biological Absorption Coefficient (BAC), Index of Bioaccumulation (BA) or Transference Factor (TF) (Kabata-Pendias 2001).

BAC values for the vines and the studied soils are shown in Tab. 4. Comparison of the values obtained for leaves with the values obtained from the literature (Kabata-Pendias 2001) allows the following conclusions to be drawn for the different major and trace elements accumulated in the different parts of the vines:

- Values obtained for the major elements that are higher than or close to 1: S (4.56), P (2.07) and K (0.88 in leaf, 0.96 in petiole and 1.01 in grape). In the case of Cs, the values are 1.2 in the leaves and petiole and 2.1 in the fruit.
- Values obtained for different elements in the range 0.1 to 1. This group includes Mg (0.48 in leaves and 0.67 in petiole), Ca (0.28) and Mn (0.13) amongst the major elements. Trace elements belonging to this class are Sr (0.70), Zn (0.37), Nb (0.23), Co (0.23), Pb (0.18), Ce (0.17), Nd (0.14) and Ba (0.14).
- Values obtained for different elements in the range 0.01 to 0.1. The major elements in this group with low BAC values are: Na (0.08), Al and Fe (0.01) and Si (0.03). The trace elements included in this group are V (0.09), Cr and Rb (0.07) and Ni (0.03).
- Peculiarities in the BAC values for the vine, in comparison to other plants, include the high affinity for Sr (the studied calcareous soils are very rich in this element) and for Fe, Ba and rare earth elements. In contrast, the vine has a very low affinity for Rb (very low content in the studied soils) and for Ni and Pb, both of which are present at very low levels in the studied plots.

The BAC values in the leaves are very similar to those obtained in the petiole and are higher than the average values for the grape in all cases.

Correlation between element concentration in soil and plant: Having described the average levels of bioaccumulation for each element, we attempted to establish a model for the behaviour of each particular element obtained in this study. This was achieved by comparing the different concentrations of elements in the soils, leaves and grapes. In general, a trace element (whether essential or not) will be accumulated in the plant according to a sigmoid-type function as its concentration in the soil is increased (Kabata-Pendias 2001).

We are aware that the number of plots used for the area is too low to establish general laws for the region. However, one of the objectives of the present study was to outline general trends in order to guide future studies on the behaviour of vines cultivated in our region for each trace element. In this sense, we established simple linear correlations (White 2009) between the content of each element in the soil and its contents in leaf and grape in vines.

The results are shown in Tab. 5. In most cases, the correlations are positive but not significant. Significant correlation does occur in leaf values for Mg, K, V, Cr, Sr and Ce, whereas for grapes the only positive and significant correlation was obtained for Sr.

We appreciate that the significant correlations for Sr and Cr are similar to those obtained for other elements such as P (White 2009) and Hg in woody species (Molina et al. 2006). In contrast, in the case of Zn it seems that a definite pattern is not obtained, as shown by the low concentration models for unpolluted soils (Madejon et al. 2003). The behaviour for Sr, Zn and Cr for the soil-leaf system is represented in Fig. 2 and in all cases a positive increasing correlation is observed.

As an example of accumulation in the fruit, we can highlight the case of Sr in Fig. 3, which again shows a positive and significant correlation.

Conclusions

From the results obtained in this study it can be concluded that novel and relevant information about the behaviour of vines cultivated in Campo de Calatrava (Subregion of La Mancha- Spain) has been obtained. The results show that the plants accumulated elements in different parts depending on the geochemical properties of the soils. This is especially evident in the case of trace elements, the presence or absence of which could show soil provenance and act as a geochemical fingerprint for the fruit. This study could be important for the chemical identification of wines produced in this region. The studied plots are representative of the area and are varied in their composition. The
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The contents of elements in the leaves of the vine variety studied (Cencibel) are comparable to the values found in the literature for major elements. Detectable trace elements include Cr, Zn, Rb, Sr, Cs, Ba, Ni, V and Ce and these are of great interest as they could represent a geochemical fingerprint for the plant.

BAC levels are similar to those reported for other plants in other parts of the world. BAC values of interest, with respect to detectable trace elements with the analytical technique used, are Sr (0.70), Zn (0.57), Nb (0.23), Co (0.23), Pb (0.18), Ce (0.17), Nd (0.14) and Ba (0.14). Elements with very low concentrations, i.e. below 0.1, are Al, Fe, V, Cr, Rb and Ni. Furthermore, the plant response to soil elements showed a significant positive linear correlation for V, Cr, Sr and Ce in leaves. For the grape, however, the only element that showed identical behaviour was Sr.

Nonetheless, further research is recommended in order to deeply study the elemental relationship between soil and vines of La Mancha region, evaluating more plots and using higher sensitive analytical techniques for some elements, such as ICP-plasma, to show a more adjusted geochemical fingerprint in the fruits.

Acknowledgements

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Reference


Table 5

Correlations between different trace and major elements in the soil-leaf system and soil-grape system, respectively. (*significant correlation is indicated in bold characters)

<table>
<thead>
<tr>
<th>System</th>
<th>Mg</th>
<th>P</th>
<th>S</th>
<th>Ca</th>
<th>Mn</th>
<th>Fe</th>
<th>K</th>
<th>V</th>
<th>Cr</th>
<th>Al</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soil-leaf</td>
<td>0.73</td>
<td>0.53</td>
<td>-0.52</td>
<td>0.67</td>
<td>0.08</td>
<td>-0.02</td>
<td>0.92</td>
<td>0.82</td>
<td>0.85</td>
<td>0.49</td>
<td>-0.23</td>
</tr>
<tr>
<td>Soil-grape</td>
<td>0.37</td>
<td>0.51</td>
<td>-0.34</td>
<td>0.44</td>
<td>0.01</td>
<td>-0.37</td>
<td>-0.16</td>
<td>-0.20</td>
<td>-0.13</td>
<td>-0.27</td>
<td>-0.52</td>
</tr>
<tr>
<td>Soil-leaf</td>
<td>0.54</td>
<td>0.10</td>
<td>0.46</td>
<td>0.03</td>
<td>0.78</td>
<td>0.38</td>
<td>-0.95</td>
<td>0.80</td>
<td>0.64</td>
<td>-0.19</td>
<td></td>
</tr>
<tr>
<td>Soil-grape</td>
<td>0.01</td>
<td>-0.10</td>
<td>0.07</td>
<td>0.42</td>
<td>0.97</td>
<td>0.57</td>
<td>-0.15</td>
<td>-0.26</td>
<td>-0.08</td>
<td>-0.07</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 2: Correlation between soil and leave contents for Zn, Cr and Sr (from left to right).

Fig. 3: Correlation of Sr content in grape and soil.

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accumulation of heavy metals in sporocarps of wild fungi. Biomet

Methods, 2

Vitis vinifera perennial grapevine (V. vinifera) in the Champagne region of

France. Environ. Pollution 156, 1092-1098.

De la Horra, J. L.; Serrano, F.; Rodríguez, J.; Hidalgo, L.;

Galgano, F.; Favati, F.; Caruso, M.; Scarpa, T.; Palma, A.;

Campos, J. A.; Tejera, N. A.; Sánchez, C. J.; González, A.; Llorens, A.; Cervera, M. L.; Armenta, S.; De la Guara,


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