Geochemistry of selected trace elements in the soil –grapevine– wine system from Huşi area (Romania)

PhD thesis summary

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The main aim of the thesis is to study the content and distribution of selected trace elements in soils and the mobility throughout the soil-plant-wine system in the vineyards of Huşi area. Knowledge of the average and the variation range of potentially toxic elements contents in soil provide information on contamination and/or pollution by comparison with the maximum permitted levels, regulated by law.

Also wine a food product, must contain these elements in a certain amount (in addition to other components and parameters such as for instance: alcooholic strength, sugar content, acidity, specific organoleptic quality category and type of wine, etc.) so consumed in moderation should not cause adverse effects on the human body.

This paper is a comprehensive and interdisciplinary study on geochemical distribution of selected trace elements in the system described by the interaction soil - plant - wine.

Among the objectives that led to the present study are:

- Determining environmental geochemical background of trace elements (Cr, Co, Ni, Cu, Zn, As, Cd, Pb) in soil;
- The amount of mobile and plant available elements: Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Cd, Pb;
- Determining the possible sources of studied trace elements;
- Determining the levels of trace elements from wine and vine leaf samples using techniques with high sensitivity (Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Cd, Pb, B, Mo);
- Comparing the result concentrations obtained in both studied wine: obtained through traditional method and commercial one with the values permitted by law.

The ways of combining the studied elements within soil constituents, plant and wine are complex and difficult to establish.

The study of the entire soil-plant-wine system is the first in Romania, which will hopefully be a starting point for future detailed studies.

It should be noted that a larger number of elements were analyzed, but for an increased clarity of this paper did not have correlations with major components, which constitute the idea of a future study.

In order to determine the trace elements contents (essential and/or potentially toxic) were used the following analytical methods: X-ray fluorescence spectrometry with energy dispersive (ED-XRF) at the Department of Geology, Faculty of Geography and Geology and coupled plasma mass spectrometry (ICP-MS) at the Institute of Geology and Mineralogy, University of Cologne where I had the honor to benefit of a training course of four months.

Overall the work is divided into five major chapters, plus an introductory part, conclusions and bibliography.

The first three chapters contain only data from the literature and the other two own contributions. After a brief introduction, Chapters I and II explain general terms and definitions of Pedogeochemistry, Agrochemistry and Viticulture, presents a short review of geochemical and agrochemical researches of the studied area, plus a geological settings and geographical framework description of the Huşi region.

Chapter III is devoted for describing soil from Huşi vineyard area. Data presented to describe the eight soil types which are classified into 6 classes are from in literature and OSPA documentations, the institution specialized for such studies in the area.

Chapter IV presents the sampling, preparation and analysis underlying this original and timely study for the Huşi area as well as nationally. It was taken samples of soil, vine leaves and grapes. From the collected grapes were obtained wine through the traditional method from the growing area of three farms belonging to SC Vincon Vrancea SA Focşani, work point Huşi, located around the city with the same name. The soil sampling was done systematically from a network of points located at a distance of about 50 meters. The soil was collected from 81 points in two depths: 0-20 and 20-40 cm from the topsoil.

For the proposed sampling (soil, vines and grapes for producing wine) were chosen plots planted with varieties of wines from the famous vineyard Huşi area: Tămâioasă Românească, Zghihară, Fetească Regală, Cabernet Sauvignon and Busuioacă de Bohotin. Leaf samples were taken in the same time with soil samples, according to the methodology described in the literature.

The color of soil samples was done by comparison with Munsell catalog. The proportion of $CaCO_3$ was carried out by using the Bernard method. For each soil sample measurements of pH (WTW Inolab 730) in aqueous solution by potentiometric method using a ratio of soil: water 2.5:1 were made. The size distribution of the soil samples was done using the LaMotte Soil Texture Unit Kit (LaMotte, USA) according to standard working method annexed thereto.

For TOC (Total Organic Carbon) and for CNS (Carbon Nitrogen Sulphur) were analyzed a number of 32 samples that was selected from the total number of collected soil samples.

The samples preparation for analysis and also the ED-XRF analysis type were conducted for all the 162 soil samples in the laboratories of the Department of Geology, "Al. I. Cuza" University of Iaşi. The pressed powder pellets necessary for analysis by X-ray fluorescence spectrometry with energy dispersive (ED-XRF) were obtained by mixing a ratio of 5:1 of soil and resin.

A total of 22 soil samples selected from the total collected samples were analyzed according to the scheme proposed by Zeien & Brummer (1991) in order to get information on the concerning chemical binding of the trace elements on the components of soil and on their availability for plant.

The soil and leaf samples were collected between July and August 2010, and grapes for wine obtained through traditional method in September of the same year. The grape samples were collected from the same plots from where the soil and leaf samples were taken so that the correlation soil-plant-wine to be relevant. The wine samples were obtained from grapes harvested in the same plots where soil and leaf samples were taken.

For each of the three parts of the studied system: soil, plant, wine the preparation manner of the samples, the analysis steps in order to perform the elemental analyses and all the used equipment are described in detail.

The transfer coefficients of wine/leaves and wine/soil were determined. The obtained values are much lower than 0.1 which do not show a direct correlation translocation of elements in the soil-plant-wine system.

A part of the powder obtained after shredding, ground and mixing of dried leaves is used later to chemical digestion for analysis of the trace elements (Cd, Co, Cu, Cr , Fe, Mn, Ni, Pb, Zn, Mo, B, As) by ICP-MS, which were determined to be pursued in the soil-plant-wine. For the plant samples, the used digestion method is wet acid decomposition in the microwave system.

The plant and wine samples has been analyzed by TotalQuant of ICP-MS method.

Romania as well as the others countries that produce and sell wine, have a rigorous national legislation that is consistent with the decisions of the International Organization of Vine and Wine (OIV).

To have a comparison with the wine found on the market, in addition to the 6 varieties of wine made from grapes harvested from the studied vineyards, other 5 different commercial wine types produced by the same company (different years of production and different vineyards) were taken to be investigated into the present study.

Chapter V, the largest chapter of the thesis is a comprehensive study of the current levels of contamination with the studied selected trace elements in the soil and vine leaf and hence wine samples, the consumer product quality. This geochemical study is accompanied by physical-chemical parameters determined on the soil collected samples.

The absorption of trace elements by roots can be both active (metabolic) and passive (non-metabolic). Besides roots, the selected trace elements can also be absorbed by the leaves. This is possible due to surface processes and atmospheric depositions on the leaves surface (mainly the contaminants).

For soil samples was highlighted an average contents for Cr, Cu and Ni exceeding the normal values allowed by law, while those of Cd, Co, Ni and Zn are below this value. In the case of Co, Ni, Zn and As values are above the normal maximum permissible soil.

A significant personal contribution is to determine the ambient geochemical background of the area and of the enrichment factor in metals and metalloids. Another important contribution is to highlight the use of sequential extraction of metals from soil likely to be available to plants. Regarding vine has shown that although potentially toxic elements (Cd, Cr, As, Pb) for both plants and humans can be found in the soil above the legal rules they do not accumulate in the leaves. This shows that the vine is not bio-accumulative.

When was compared the commercial wine with traditional wine (which was obtained without the use of mechanical devices, additives or chemical treatments differences), were observed differences for all studied traces elements. A first observation is an obvious enrichment of trace elements in the commercial wines comparing to those obtained manually from grape juice, under natural conditions and without any specific treatment. Exceptions are in the cases of

Cu and B elements, when the wine produced from grapes grown in studied vineyards has concentrations higher than those of the commercial wines.

Along with other environmental factor conditions favorable from Huşi area (geology, relief, climate), the characteristics of the studied soil are optimal to compile the terroir" composition " from the Huşi area as: clay and sandy medium texture, a soil reaction from slightly acid to slightly alkaline, with low fertility indicated by low values of C/N ratio and % TOC. The obtained data by ED-XRF analysis, combined with those obtained from the University of Cologne, Germany using ICP-MS technique have led to objectives for this study:

- Knowledge of the local ambient geochemical background is a new national issue for vineyard soils, even if is on a small area as Huşi vineyard.

The current legislative of normal soil values for the Cr, Cu, Ni, Pb and As elements exceeds the range of the ambient background values that need to be taken into account for the maximum allowable established values for a locally . The actually Romanian legislation provides no explanation for settings of the normal, maximum or warning imposed limits and therefore the ambient geochemical background knowledge on local or regional area is an important aspect that should not be overlooked for the categorizing of soils as unpolluted, contaminated or polluted. At the same time it is advisable to take into account the potentially toxic trace elements amounts for plants and people.

- Determination of the mobile part of studied trace elements provides information on how the total amount of soil is available for plant and is potentially available as being useful for future applications of the amendments, to maintain a control of the mobile part of the trace elements so that do not reach up the toxic levels for normal growth of plant.

The importance for this study is to highlight that although the total contents of some studied trace elements (Cr, Cu, Ni, Pb, As) exceeds the normal values required by law, the quantity available (mobile) for plant is much lower. Data from this study cannot be carried back to the history of the vineyard because of the applied treatments which were changed from year to year, from plot to plot using different products (with different percentages of major and minor elements or of the accessory compounds). In the investigated area, the vineyards are over 40 years old and there are no comparative values so that the obtained data can be considered as a benchmark for future studies.

- Determining the ranges of the 12 elements for soil (along with estimating of the mobile part), plant and wine samples was made possible by the use of special equipment for the chemical elements presents in small quantities;

The obtained results on the leaf and wine samples using ICP-MS method are very helpful both from the point of view of the opportunity to describe the range orders of the studied trace elements contents and of being the first national study on this subject.

For the case of soil samples, the ICP-MS analysis is a way of validation by external control of ED-XRF analyzes.

The ways of combining the studied trace elements of soil constituents, plant and wine are complex and difficult to establish. The translocation coefficient from soil to plant and the derived correlations reveals distinct sources of elements: the bioavailable trace elements from soil solution are absorbed by the plant roots and transported with water and strain every raw sap to the other organs of the plant or it can be adsorbed on the leaf level, where can be because of the foliar treatments used in viticulture or from atmospheric deposition, but this coefficient gives no indication of the quantities.

The obtained results for the wines produced traditionally from grapes harvested from the Huşi area and for the commercial wines could be compared with the maximum values for the five trace elements (Cu, Zn, As, Cd, Pb) allowed by the Law no. 1134/2002. Compared with other types of wines from trade areas and different years, the traditionally obtained wines contain the studied trace elements in much smaller quantities. This can be attributed to the precipitation of the biggest amount of these trace elements with wine yeast, but cannot be correlated to indicate a "more" good wine because of their different year of production and the different applied treatments to the commercial wines for clarification and conservation.

Besides the bioavailable trace elements from soil necessary for the proper growth and development of the vine (as Cu, Zn, Mn, Fe), the elements with toxic effects on plants as Cr, Cd, Pb, Ni, As or even the neutral one, Co (with no effect on plant nutrition) there are a number of other factors unaccounted in this study that could influence the quality of wine: rainy and dry time during that year, the amount of sugar contained by grapes, the vine diseases (mildew, rot) or other effects that may occur after the fermentation of must (vinegar, copper or ferric disposal, mold taste, color change and so on).