Journal of Geochemical Exploration xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

Journal of Geochemical Exploration

journal homepage: www.elsevier.com/locate/gexplo

Influence of the soil pH in the uptake and bioaccumulation of heavy metals (Fe, Zn, Cu, Pb and Mn) and other elements (Ca, K, Al, Sr and Ba) in vine leaves, Castilla-La Mancha (Spain)

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ARTICLE INFO

Article history:
Received 24 July 2015
Revised 10 November 2015
Accepted 24 December 2015
Available online xxxx

Keywords:
pH
BAC
Mineral elements
Vine

ABSTRACT

Each soil–plant system has specific parameters on the uptake of different minerals in the soil, depending on several factors. One of these factors, perhaps the most important, is the pH. The aim of the work described here was to ascertain the role of pH in the uptake of some mineral elements, including heavy metals. For this purpose, 101 vineyard plots have been selected in Castilla-La Mancha (Spain) and soils and leaf samples have been analysed by the XRF technique. The BAC (biological absorption coefficient) was also calculated. The behaviour observed for some of the studied elements was different in acidic and alkaline soils: Copper (Cu) and calcium (Ca) had high BAC values in alkaline soils (1.87 and 0.99, respectively) and in acidic soils (4.67 for Ca and 2.24 for Cu); in alkaline soils iron (Fe) and aluminium (Al) had the same BAC value (0.02). Barium (Ba) and lead (Pb) showed similar values in both cases (0.20 in acidic soil and 0.26 in alkaline soil for Ba; 0.15 in acidic soil and 0.29 in alkaline soil for Pb). In contrast, strontium (Sr), zinc (Zn) and manganese (Mn) were preferentially bioaccumulated in acidic soils (1.01, 1.00 and 0.50 respectively). Mineral elements are accumulated in the leaves of vines depending on the soil pH. The pH influences the ionic form in which the element is present in the soil.

1. Introduction

The vine is one of the most important crops in Castilla-La Mancha (about 500,000 ha) and the wine sector is of major importance for the economy of the area (Amorós et al., 2013). Mineral nutrition is a crucial factor to improve the vine culture (Romero et al., 2014). Several authors (Kabata-Pendias, 2001; Marschner, 2012; Wild, 1992) have studied the uptake and bioaccumulation of mineral elements in plants. The uptake of mineral elements in each soil–plant system depends on several factors and, as a consequence, knowledge of the geochemical soil properties helps in the evaluation of both fertility and pollution threats. At the same time, it can be stated that the composition of the soil (Protano and Rossi, 2014; Rogiers et al., 2006) should generally influence the composition of plant products (Censi et al., 2014; Chopin et al., 2008; Kabata-Pendias, 2001; Pessanha et al., 2010). Changes in bioavailability of mineral elements are increasingly important due to environmental regulations (Hamon et al., 2006; Gómez-Armesto et al., 2015).

Soil pH is one of the most frequently measured parameters (Wild, 1992) because it is considered to be a good indicator of a range of chemical properties (McLean, 1982). The pH influences, both directly and indirectly, the behaviour of the chemical elements in the soil (Shaheen et al., 2013; Teng et al., 2015). Soil pH also influences the bioavailability of chemical elements in the soil (Hamon et al., 2006; Jackson, 2008; Likar et al., 2015) and plays an important role in their availability and toxicity for plants (Kabata-Pendias and Mukherjee, 2007). The soil concentrations and availability of minerals elements for plants generally decrease as the pH and calcium content increase (Pérez-de-los-Reyes et al., 2013; Wild, 1992). The bioavailability of Cu, Zn, Ni, Cd and Pb is significantly reduced in soils with a pH above 7 (Han, 2007). Besides, root exudates can induce changes in the pH of rhizosphere and this fact might influence the availability of mineral elements (Kidd et al., 2009).

Absorption of various elements by the roots is related to mass flow mechanisms and complex diffusion changes (Marschner, 2012). Essential trace elements play a role in plant development and are found in soils in different chemical forms (Azcón-Bieto and Talón, 2008; Guardiola and García, 1991). Heavy metals are an increasingly serious problem for soil quality and their presence in soil is strongly influenced by anthropic activities (Teng et al., 2015). Soils contaminated with

Abbreviations: BAC, Biological absorption coefficient; CLM, Castilla-La Mancha.
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http://dx.doi.org/10.1016/j.gexplo.2015.12.012
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heavy metals pose an increasing risk to human health (Rascio and Navari-Izo, 2011).

Ca and K, as macronutrients, have a significant direct effect on the growth and physiology of the grapevine (Baker and Pilbeam, 2007). Fe, Zn, Mn and Cu are essential micronutrients for the plant. Mn has an important role in the synthesis of chlorophyll and in nitrogen metabolism (Likar et al., 2015; Marschner, 2012) and it is present in soil as exchangeable Mn or Mn oxide (White et al., 2012). Fe is characterized by the ease with which its oxidation state changes (Marschner, 2012) and it therefore plays an important role in electron transport processes (Baker and Pilbeam, 2007). Zn is linked to enzymes and participates in three plant functions: catalytic, coercive and structural (Navarro, 2003). Cu, like Fe, participates in electron transfer reactions and it is an essential microelement, although at high concentrations it can be toxic for plants and humans (Gómez-Armesto et al., 2015).

Sr and Ba are the trace elements (not essential nutrients) found at the highest concentrations in the soils of the region (Jiménez-Ballesta et al., 2010). The soils contain an average of 10% total Al (Kabata-Pendias, 2001) and under acidic conditions this element can be solubilized and taken up by the plant. Pb is a trace element that is highly influenced by environmental conditions (Chopin et al., 2008).

The ability of the plant to uptake nutrients can be measured by the bioaccumulation coefficient (BAC), which is calculated as the ratio between the concentration of the element in the plant and its content in the soil (Kabata-Pendias, 2001). This coefficient can be measured in any plant tissue (root, leaf or fruit) regardless of the availability of the element in the soil. Some BAC data have been reported in specific studies on vine by Amorós et al. (2012, 2013), Pérez-de-los-Reyes et al. (2013) and Bravo et al. (2015).

The aim of the work described here was to evaluate how some heavy metals (Fe, Zn, Cu, Pb and Mn) and other elements (Ca, K, Al, Sr and Ba) accumulate in the leaves of the vine depending on soil pH. The question to address in this respect is: Are there differences in absorption between acidic ($pH < 7$) and alkaline ($pH > 7$) soils?

2. Material and methods

A total of 101 soil and leaf samples were taken from different wine-growing areas of Castilla-La Mancha (Fig. 1). The profiles were opened using a Caterpillar machine. The soils were described according to the criteria defined by FAO-ISRIC-IUSS (2006).

Leaf samples were also taken from vine plants (Tempranillo variety and 110 Richter rootstock; more than ten years old vineyards; traditional tillage management; and vsp trellis system were preferably chosen) in the same areas from which the soil samples had been obtained. In each plot, 20 mature leaves were collected before harvest according to the methodology suggested by Ernst (1995). In the laboratory the leaf samples were dried in an oven for 7 days at 36 °C.

The soil reactivity (pH) was measured in a 1:2.5 aqueous extract in water using a GLP 22 pH meter (Porta et al., 1986). The trace elements were studied by grinding samples in an agate mortar until the material had a diameter of less than 43 μm. The samples, both soil and leaves, were analysed by X-ray Fluorescence using a Philips PW 2404 spectrophotometer with a maximum power of 4 kW (set of crystal analysers for LiF220, LiF200, Ge, PET and PX1, flow detector and twinkle detector). Analysis of the samples was carried out with pearls of lithium borate. Quality control was evaluated by duplicate analysis of certified reference samples (BCR 62, SMR 1573a, SMR 1515).

The bioaccumulation of the elements in the leaves was evaluated by calculating the Biological Absorption Coefficient (BAC). The BAC is the ratio between the concentration of the element in the plant (root, leaf or fruit) and the element concentration in the soil (Kabata-Pendias, 2001).

$$BAC = [leaf]/[soil]$$

All of the mathematical and statistical computations were carried out using IBM SPSS Statistics 19 and Microsoft Office Excel, under licence to the University of Castilla-La Mancha.

3. Results and discussion

3.1. Metal contents in soils and leaves

The average results obtained for mineral element contents in soil and leaf are given in Table 1. It can be seen from the values reported for the soil that Ca is the most abundant element (108.7 g kg^{-1}) with values that are higher than world levels (15.00 g kg^{-1}). The values obtained for K (16.36 g kg^{-1}) are slightly higher than the world average (14.00 g kg^{-1}). The opposite trend was found for Fe (22.06 vs. 40.00 g kg^{-1}), Mn (0.38 vs. 1.00 g kg^{-1}), Al (53.96 vs. 71.00 g kg^{-1}) and Zn (32.57 vs. 78.50 g kg^{-1}).

Sr is the predominant trace element in the studied soils (241.88 mg kg^{-1} vs. 220.0 mg kg^{-1} in the world) and the second most abundant is Ba (191.8 mg kg^{-1} vs. 513.0 mg kg^{-1}). This relative order of abundance is opposite to that reported by Jiménez-Ballesta et al. (2010) for soils of Castilla-La Mancha. The Pb concentrations determined in the studied soils are lower than the average reported in the

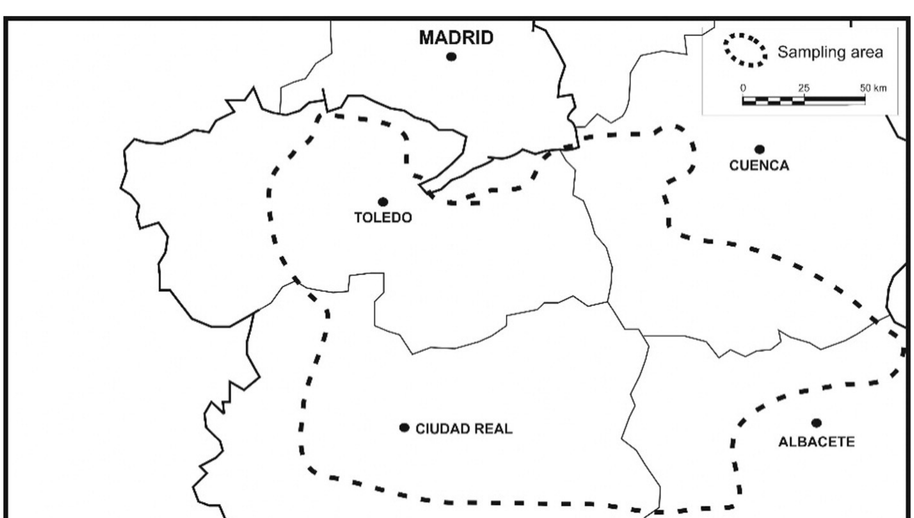

Fig. 1. Location map of the studied area.