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# Copper accumulation regarding the soil characteristics in Sub-Mediterranean vineyards of Slovenia

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#### Abstract

Copper accumulation in vineyard's soil is the consequence of long-term use of copper-based fungicides against downy mildew. Copper contamination in soil of 22 vineyards in the Sub-Mediterranean winegrowing region has been studied in terms of various soil properties (cation exchange capacity, organic matter and pH), vineyard age, soil depth and landform. The CaCl<sub>2</sub>/H<sub>2</sub>O extractable Cu and total Cu content were determined. The study has demonstrated that the landform had an impact on CEC and pH, but it did not influence organic matter content. The CaCl<sub>2</sub>-extractable Cu showed that the concentration obtained were low in all soil samples and ranged between 0.04 to 0.08 mg kg<sup>-1</sup>. The highest total Cu content in soil was determined on terraces (110–120 mg kg<sup>-1</sup>), followed by plateaus (83–93 mg kg<sup>-1</sup>) and planes (71–89 mg kg<sup>-1</sup>), but in forests (62–65 mg kg<sup>-1</sup>). Cu content increased with the vineyard age, except for planes, and it decreased with soil depth. The Slovenia guidelines for the assessment of contaminated sites recommend that total Cu concentrations in soil that exceed 60 mg kg<sup>-1</sup> require environmental analysis. This level is exceeded in all of the studied vineyards. Although our results indicated a lower extent of Cu accumulation in comparison to some other well-known winegrowing regions (Bordeaux 800 mg kg<sup>-1</sup>; Trentino Alto Adige 161 mg kg<sup>-1</sup>, etc.), the results highlighted that spraying with copper-based pesticides in future should be limited.

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### 1. Introduction

The sources of copper in soil are parental material (Tiller, 1983) and anthropogenic impact through spraying and fertilization (Lund, 1990). Since the end of the 19th century, the mixture of copper sulphate and lime (called Bordeaux mixture) has been extensively applied and it is still in use (Baker, 1993; Besnard et al., 1999). Because of its worldwide use, the accumulation of copper has already been established in some viticulture soils (France: Bordeaux 800 mg kg<sup>-1</sup>, Alsace, Burgundy and Champagne 400–500 mg kg<sup>-1</sup>; Italy: Valle d'Aosta 300 mg kg<sup>-1</sup>, Lombardia 260 mg kg<sup>-1</sup>, Trentino Alto Adige 161 mg kg<sup>-1</sup>, Piemonte 90 mg kg<sup>-1</sup>, Tuscany 34 mg kg<sup>-1</sup> etc. (Brun et al., 1998)), where influences plant growth, micro organisms and soil chemical properties (Merry et al.,

1983; Flores-Veles et al., 1996; Besnard et al., 1999). Pietrzak and McPhail (2004) mentioned that the conversion between copper fractions is slow, indicating that Cu can stay active in soils for long periods of time, greater than tens of years, and may result in leaching and transport to deeper soil layers. Pietrzak and McPhail (2004) cited that the source of Cu in soils and the content of organic matter have influenced the Cu distribution among various soil fractions. Potentially available Cu in vineyard soils constitutes more than 60 wt.% of total Cu in the upper part of soil profiles and the percentage decreased with increasing depth. Cu in uncontaminated soils existed mainly in less mobile fractions, whereas potentially available Cu constitutes approximately 10 wt.% of total Cu content throughout soil profiles (Pietrzak and McPhail, 2004).

Furthermore, it is also well-known that transition metals in soil are present in different chemical forms which in turn have an impact on their mobility and bioavailability (Marschner, 1995), particularly through physical-chemical characteristics of

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soil (Boon et al., 1998; Wenger and Grupta, 1998; Alva et al., 2000; Rusjan et al., 2006). Brun et al. (2001) citied that the Cu content in roots of plants increased with increasing total Cu constant in the soil and with decreasing soil CEC. Cu accumulation in roots may be as high in calcareous soils as in acid soils, suggesting that soil pH had little influence. Brun et al. (2001) in the case of the vineyards mentioned that aerial parts of the plants would not be a good indicator of plant Cu uptake, as it provides no insight into the real amount of Cu transferred from the soil to the plant. High Cu concentrations in the soil influenced low survival, low total plant biomass, delay in flowering and fruiting, and low seed set, but the contrasting effects on patterns of resource allocation depending on the plant species (Brun et al., 2003). Also Chaignon et al. (2003) confirmed the bigger sensitivity of Cu contents in roots compared to Cu in shoots, where strong positive correlations were found between root Cu concentration, total soil Cu and organic C contents especially in calcareous soils, suggesting a prominent role of organic matter in the retention and bioavailability of Cu. Such relations were not observed when including the five acidic soils in the investigated population, suggesting a major pH effect (Chaignon et al., 2003).

The region of Sub-Mediterranean in Slovenia has enjoyed a long tradition of intensive grapevine growing, with frequent use of copper containing fungicides. The reasons for their frequent use lie in high air humidity and temperature typical of the period of vine growth. Therefore, the official policy is to restrict such practice by introducing integrated pest management in vineyards and biological grape production. Taking this into consideration, the limit of 5 kg of copper per hectare per year has been set (Directives of Integrated, 2006).

The results of our study on copper content and accumulation in vineyard soils from Sub-Mediterranean winegrowing region in Slovenia are presented in relation to soil depth, age of vineyard and landform.

# 2. Materials and methods

### 2.1. Sampling sites and soils

The Sub-Mediterranean winegrowing region of Slovenia has a traditional and specific viticulture, where vineyards are mainly terraced on slopes slanted over 30%. One hundred winegrowers cultivate vine on 1810 ha of land, which is subdivided into 4 winegrowing locations due to different soil types and macroclimatic conditions (Rusjan and Korošec-Koruza, 2003). The landscape consists of three landforms: the terraces (1295 ha at inclination higher than 15%), plateaus (315 ha at inclination lower than 15% and up to the altitude of 80 m) and planes (200 ha in river valleys at the altitude between 20 and 50 m). The major differences among landforms lie in their soil types and inclination. Terraces and plateaus are made mainly of Eocene calcareous soils called flysch (marls and sandstones) with poorly differentiated profiles, anthropogenised soils (vitisol), texture, extremely heavy to light soil which dries and heat out fast and is subject to water erosion. The planes consist of alluvial and coluvial soils with active lime and high levels of groundwater. They retain more moisture, the temperature change is slower (Stritar, 1991; Table 1).

The climate is Sub-Mediterranean, with frequent dry periods in summer and an average annual rainfall of 1200 mm. Heavy storms are recorded in summer. They are responsible for severe soil erosion as well as for the transport of suspended matter (Ribolzi et al., 1996).

## 2.2. Soil sampling

Soils were sampled from 22 vineyards (within the latitude  $45^{\circ}57'$  and  $46^{\circ}01'$  (North) and within the longitude  $13^{\circ}30'$  and  $13^{\circ}33'$  (East)) (Table 2) which were selected according to age, soil depth and landforms. In addition, the samples were collected from one permanent forest and one ex vineyard parcel simultaneously in order to estimate the background copper content and corresponding soil properties. At each location, the soil was collected at three depth levels: 0-20 cm, 20-40 cm and 40-60 cm. Twenty sampling points per hectare were chosen randomly within each site. In order to obtain an average sample, the particular depth level of each sampling point was combined with the rest from the same vineyard, airdried at 40 °C, and thoroughly homogenized. Per vineyard, three samples were thus obtained, altogether 72 samples (24 sampling locations, 3 depths).

The vineyard soil samples were grouped into 4 different classes according to the vineyard age: less than 5 years, between

Soil identification and description (Stritar, 1991; FAO, 2001)

Soil unit	FAO classification	Factor description		Morphopedological	Most
		Internal	External	unit	frequent use
Saturated soil	Calcaric Leptosol	Active lime,	Exposure,	Plateaus,	Vineyards,
		Appearance of Sandstone	Access,	Terraces	Forests,
			Relief		Pastures
Anthropogenized soil (rigosol)	Anthrosol	Larger mineral	Access,	Terraces	Vineyards,
		particles,	N/S exposure size of terraces		Orchards,
		Active lime			Nurseries
Coluvial soil	Calcaric Regosol	Active lime,		Planes	Vineyards,
Alluvial soil		Groundwater			Orchards,
					Horticulture,
					Lucerne

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