EFFECT OF SOIL PARTICLE SIZE ON COPPER AVAILABILITY

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ABSTRACT

This paper deals with the effect of soil particle size on copper availability. Twelve vineyards, (at three depths) all on the territory of the Vojvodina Province, were observed for soil contamination with copper. Soil samples were taken in four locations (5 soil types). The samples were analyzed for total copper and available copper (in EDTA). and sequential extraction was conducted. Correlations between soil particle size and copper fractions were calculated and analyzed. The obtained results indicated that the increase in the portion of smallest soil separates, clay and silt, tended to reduce copper availability, whereas the larger separates tended to increase it. The available fractions, Cu_{EX} and Cu_{CAR}, were significantly negatively correlated with the content of clay and silt along the entire soil profile of the analyzed vineyards. Simultaneously, these two factions were positively correlated with the content of fine sand, also along the entire soil profile. The results confirmed that, when assessing the extent of soil contamination with copper, soil mechanical composition should be taken into account as an important factor of copper availability.

INTRODUCTION

Worldwide studies of copper levels in vineyard soils have shown that the use of copper-based pesticides constitutes a serious risk, although until recently the use of such pesticides was considered safe compared with other pesticides (Dixon, 2004; Komarek et al., 2010). When assessing the risks of copper pollution of soil, it is important to know its geochemical (mobility, reactivity) and biological properties (availability, toxicity) (Kabat-Pendias, 2004; Menzies et al., 2007). Previous studies (Kabat-Pendias and Pendias, 2001) have shown that the content of clay is crucial for copper availability. Parat et al. (2002) detected higher copper contents in silt and clay than in coarse and fine sand.
In the research of Besnard et al. (2001), the largest portion of copper was detected in the clay separate of soil and in POM. High copper availability was determined in arenosol (Ninkov et al., 2009).

MATERIALS AND METHODS

Soil samples were taken from individual vineyards from all three grape-growing regions of the Vojvodina Province: Srem - the locations of Sremski Karlovci and Banoštor (45° 11' N, 19° 55' E and 45° 11' N, 19° 36' E, respectively), south Banat - the location of Vršac (45° 06' N, 21° 20' E), Subotica-Horgos sands - the location of Hajdukovo (45° 11' N, 19° 55' E). A total of 12 vineyards were observed from which 36 soil samples were collected.

Data were statistically processed using STATISTICA for Windows version 8.0 (StatSoft, 2007).
The samples were air-dried and milled to a particle size of <2 mm, in accordance with ISO 11464:1994.
Particle size distribution was determined in the <2mm separate by the internationally recognized pipette method. The sizes of particles were defined as coarse sand (200-2000 μm), fine sand (20-200 μm), silt (<20 μm) and clay (<2 μm).
Total Cu content in soil samples was measured after digestion with aqua regia (1 HNO_3:3 HCl), in accordance with ISO 11466:1995. Total Cu concentration was determined by ICP-OES (Vista Pro-Axial, Varian). Quality control was carried out periodically with IRMM BCR reference materials CRM-141R and CRM-142R for aqua regia digestion. Deviations were within ± 10% of the certified values.
EDTA-extractable Cu was determined by the EDTA extraction protocols for IRMM BCR reference materials CRM-484: 5 g soil/50 ml EDTA concentration 0.05 mol/L pH=7.00, with the extract being used to determine the Cu content on a Varian AAS Spectra AA 600 flame system. Quality control was carried out periodically with IRMM BCR reference materials CRM 484. Deviations were within ± 10% of the certified values. EDTA-extractable Cu was regarded as an indicator of the plant-available fraction of soil Cu (Chaignon et al., 2003).
Sequential extraction of Cu was performed by the method of Tessier et al. (1979). Five individual copper fractions were determined: 1. Cu_{EX} (exchangeable), 2. Cu_{CAR} (bound to carbonates), 3. Cu_{FeMnOx} (bound to Fe and Mn oxides), 4. Cu_{OM} (bound to organic matter) and Cu_R (residual).
Copper concentrations were determined by ICP-OES (Vista Pro-Axial, Varian).

RESULTS

According to the content of total copper, Cu_T, the examined vineyard soils were found to be contaminated by copper as a result of long-term application of copper-based fungicides. Of the 36 samples analyzed, 26 of them had the Cu concentration above the critical level of 60 mg/kg (Scharmel et al., 2000). The average Cu_T content of 89.9 ± 45.1 mg/kg was also above the critical level. Twelve samples had the Cu_T content over the MAC of 100 mg/kg (Official Gazette of the Republic of Serbia, 23/94).
The mechanical composition of soil in the studied vineyards varied in dependence of the different soil types in the observed locations. In the location of Sremski Karlovci, the soil type was rendzina. Its clay-silt-sand separates ranged around 20%, 40%, and 40%, respectively, which is considered as a "balanced structure" ideal from the agronomic point (Vučić,1987) .
In the location of Banoštor, with the chernozem soil, the clay content was increased (about 30%), at the expense of a reduced content of silt (about 30%). In the location of Vršac, skeletal plot was present in some parts of the vineyard. The percentage of rock fragments ranged from 8.5% to 57%. Two soil types were identified in that location, vertisol and regosol. In the location of Hajdukovo, the soil type was arenosol and all samples belonged to the texture class of loamy fine sand. The portions of clay and silt were small (<5%) while the portion of fine sand ranged from 55% to 94%.
The sum of the first two fractions in the sequential analysis is considered as the content of available copper: exchangeable (Cu_{EX}) and copper bound to carbonates (Cu_{CAR}). The content of available copper (Cu_{EX}+Cu_{CAR}) is highly correlated with Cu_{EDTA}, r = 0.81.
According to Karczewska (1996) (cit. Pieterzak and McPhail, 2004), the fractions Cu_R and Cu_{FeMnOx} are the least active and they have the lowest impact on living organisms. The

fractions Cu_{OM} and Cu_{CAR} are sensitive to changes in soil conditions, such as organic matter demineralization, or changes in redox potential and pH, which may increase their mobility.
In this study, the largest portion of copper was located in non-available fractions, which was in agreement with literature data (Scharmel et al., 2000; Chaignon et al., 2003; Pieterzak and McPhail, 2004; Fernandez-Calvino et al., 2008; Komarek et al., 2010).
As stated in literature (Adriano, 2001; Kabata-Pendias and Pendias, 2001), the mechanical composition of soil, i.e., the portion of clay, had a decisive impact on copper availability. In the analyzed vineyard soils, copper availability was reduced as the clay content increased along the entire soil profile.

Table 1. Correlations between different copper fractions and soil separates in the layer 0-15 cm

Soil depth 0-15cm	Clay (<2 μm) %	Silt (<20 μm) %	Fine sand (20-200 μm) %	Coarse sand (200-2000 μm) %
Cu_{EX} %	-0.88**	-0.83**	0.94**	0.67*
Cu_{CAR} %	-0.65*	-0.72**	0.78**	0.47
Cu_{FeMnOx} %	-0.31	0.09	0.05	0.21
Cu_{OM} %	0.20	-0.31	-0.13	0.37
Cu_{R} %	0.33	0.55	-0.33	-0.59*
Cu_{T} mg/kg	0.56	0.36	-0.60*	-0.19
Cu_{EDTA} mg/kg	0.29	0.03	-0.29	0.06
$Cu_{EDTA/T}$ %	-0.78**	-0.90**	0.92**	0.65*

* $p \leq 0.05$; ** $p \leq 0.01$

The available fractions Cu_{EX} and Cu_{CAR} were significantly negatively correlated with the contents of clay and silt along the entire profile of vineyard soil ($p < 0.01$), except for the correlation between Cu_{CAR} and the clay content in the 0-15 cm layer ($p < 0.05$). On the other side, these two Cu factions were positively correlated with the content of fine sand, also along the entire profile ($p < 0.01$; Table 1). The content of Cu_{EX} was positively correlated with the coarse sand separate in the soil layers 0-15 and 30-60 cm. The indicator of copper availability, $Cu_{EDTA/T}$ showed the same significant correlations as the exchangeable fraction (Cu_{EX}) except for the clay content in the layer 30-60 cm, where the correlation was nonsignificant (Table 1). The obtained results indicated that copper availability went down as the portion of the finest soil separates, clay and silt, increased, while it went up with th eincrease in the portion of the coarse separates. The positive correlation ($p < 0.05$) between the residual copper (Cu_{R}) and the content of silt in the layer of 15-30 cm also confirmed this pattern. In a study of calcareous vineyard soils (Parat et al. 2002), copper content was higher in the silt and clay separates than in the coarse and fine sand.
Also, the negative correlation ($p < 0.05$) between the portion of fine sand and Cu_{T} in the surface layer of the vineyard soil indicated that all other copper fractions were prone to leaching in soils of light mechanical composition.

CONCLUSIONS

- Estimated on the basis of the content of total copper (Cu_{T}), the vineyard soils were contaminated by this element as a result of a long-term application of copper-based fungicides. The average value of Cu_{T}, 89.9 ± 45.1 mg/kg, was above the critical level. Values over the MAC were recorded in 12samples.

- The available copper fractions and availability indicators were significantly negatively correlated with the portion of clay particles and also positively correlated with the portions of fine and coarse sand. These values confirmed that copper is less mobile in soils with a high portion of clay.
- The obtained results confirmed that, when assessing the risk of soil contamination with copper, it is necessary to analyze the mechanical composition of soil as an important factor in its accessibility.

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