

COPPER ACCUMULATION AND AVAILABILITY IN VINEYARD SOILS OF SERBIA

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Abstract. *The focus of this work is to measure the accumulation and distribution of copper in vineyard soils in Serbia as a step towards understanding copper existence in soils and its potential for availability to flora and fauna. Several single extractions are performed in parallel to the determination of total copper content after aqua regia digestion. The use of copper-based fungicides in Serbia has increased the total copper concentration in some vineyard soils to 430 mg kg⁻¹ compared to background levels of approximately 30 mg kg⁻¹. Total copper concentration has varied considerably but exceeded 100 mg kg⁻¹ (national limit) in 62% of the examined soil samples. The copper distribution in the examined samples is different, the amounts of Cu extracted by the various extractants ranged as follows, when expressed relative to the total Cu content in the soils: 0.8-8.8% for NH₄OAc and 5.8-44.4% for EDTA. The study shows that copper can stay active in soils for long periods of time, longer than ten years, and may result in leaching and transfer to deeper soil layers.*

Key Words: *copper, accumulation, availability, vineyard soil*

1. INTRODUCTION

Since 1885, copper salts (Bordeaux mixture, Ca(OH)₂+CuSO₄) have been widely applied as fungicides against mildew of grape vine. A substantial proportion of added copper sulphate sprayed annually on the vines reaches the soil, where it often remains fixed in the surface layer [1]. The worldwide use of copper based fungicides has resulted in copper accumulations in some agricultural soils far in excess of trace amounts that are required for healthy plant growth, and numerous studies have indicated that prolonged use of copper-based chemicals often results in soil contamination [2, 3].

Despite its environmental and agricultural importance, the concentration, distribution and fractionation of both anthropogenic and naturally occurring copper in soil is poorly

known. Although the total copper content in soils is a useful indicator of soil deficiency and/or contamination, it does not provide enough information about its environmental impact. Copper availability to biota (as a nutrient or toxin) and its mobility are the most important factors to be considered when assessing its effect on the soil environment. To understand the behavior of Cu in soils, it is important not only to measure total concentration but also to study Cu distribution, using physical and chemical techniques [4, 5].

In this paper we present some of the results of our studies of copper in soils from selected regions of Serbia. The aim of this work is to study copper accumulation and distribution by aqua regia digestion and single extraction procedures, in order to gain information about the plant availability and mobility.

2. MATERIALS AND METHODS

Soil samples are collected at various locations within vineyard plots (or former vineyard soils) (Fig. 1) and cover a large range of total Cu content. In all vineyards, soil samples are collected as close to the vine lines as possible and in the middle of the row, between two sampled lines. Fungicide usage is variable annually as well as between vineyards. The parcel from location 2 has not been treated for the last ten years, and from location 4 for the last two years. Sample 3 is from the former vineyard where after the vine plantation, the soils are ploughed to 50 cm depth.

The 0-2, 2-20 and 20-30 cm layers are sampled to assess the distribution of Cu with depth. Soil samples are air-dried and sieved at 2 mm prior to being used for subsequent analysis. Physical and chemical properties and total copper concentrations are measured in soil samples including vineyard soils and adjacent background soils. The organic matter content is determined as a weight loss after heating at 500°C for 2 h; pH measurements are carried out in deionized water (100 ml), after stirring the air dried sample portion of 20 g for an hour. The total soil Cu content is determined by aqua regia digestion (HCl/HNO₃ 3:1 v/v). Several single extractions are performed in parallel to the determination of total copper content. Three methods are used for evaluating soil-available Cu:

1. EDTA extraction: 7.5 g of soil is extracted with 50 ml of Na₂-EDTA 0.01 M + CH₃COONH₄ 1 M for 2 h at 20°C under stirring, prior to being filtered;
2. NH₄OAc extraction: 5 g of soil is extracted with 100 ml of CH₃COONH₄ 1 M for 1 h at 20°C under stirring, prior to being filtered; and,
3. CaCl₂ extraction: 5 g of soil is extracted with 50 ml of CaCl₂ 0.01 m for 2 h at 20°C under stirring, prior to be filtered.

The first extraction is done with a solution of 0.01 M Na₂-EDTA/ammonium acetate (pH=7), as an indicator of the plant available fraction of soil Cu [6]. The water soluble and exchangeable fractions are determined by 1 M CH₃COONH₄ [7]. In addition, Cu is extracted with 0.01 M CaCl₂ in order to estimate the exchangeable fraction of soil Cu [8]. Concentration of Cu in soil extracts are determined by flame atomic absorption spectrometry (AAS).



Fig. 1 Location of the sampling sites; (samples 1, 2, 3-Grocka; sample 4-Zemun; sample 5-Indjija; sample 6-Vrsac; sample 7-Aleksandrovac)

3. RESULTS AND DISCUSSION

Soil pH, total Cu content and extractable Cu content of 7 soils are presented in Table 1. The pH-H₂O value was neutral or subalkaline. The amount of Cu extracted by CaCl₂ is very low; in all samples it is below the detection limit of AAS (0.1 mg l⁻¹). Organic matter contents are given in Table 2.

The amounts of total Cu vary considerably, ranging from 24.9 mg kg⁻¹ in sample 3, which is close to normal, geochemical background level of this region (22.6 mg kg⁻¹), to 432.8 mg kg⁻¹ in sample 5, which is fairly large (about 10-fold larger) compared with the background value (41.1 mg kg⁻¹). So do the amounts of Cu extracted by the various extractants ranged as follows, when expressed relative to the total Cu content in the soils: 1.6-8.8% for NH₄OAc (excluding sample 2) and 5.8-44.4% for EDTA (Fig. 2). 62.5% of the analyzed soil samples exceed the maximum concentration (100 mg kg⁻¹) established for soil by the national legislative [9].

Table 1 Soil pH, total Cu and extractable Cu of the 7 soil samples (mg kg⁻¹)

Sample	Depth (cm)	pH (H ₂ O)	Total	EDTA	NH ₄ OAc
1 Grocka	0-2	7.4	166.3	49.3	4.1
1	2-20	7.6	94.5	28.9	2.5
1	20-30	7.5	94.5	26.3	2.4
2 Grocka	0-2	8.0	79.9	17.1	ND
2	2-20	7.7	105.9	22.8	ND
2	20-30	8.1	82.1	17.9	ND
3 Grocka	0-2	7.7	43.6	8.4	1.4
3	2-20	7.9	49.8	10.1	1.5
3	20-30	8.0	24.9	5.1	1.8
4 Zemun	0-2	7.6	109.5	31.1	2.7
4	2-20	7.2	102.3	20.8	1.8
4	20-30	7.3	94.2	20.5	1.5
5 Indjija	0-2	7.3	100.5	5.8	2.4
5	2-20	7.5	358.2	45.2	11.0
5	20-30	7.4	432.8	59.9	12.2
6 Vrsac	0-2	7.6	134.1	57.5	11.4
6	2-20	7.5	146.7	65.1	12.4
6	20-30	7.8	113.1	45.5	10.0
7 Aleksandrovac	0-2	7.2	180.5	58.7	13.6
7	2-20	7.5	300.1	92.7	24.2
7	20-30	7.3	366.0	92.1	25.2

ND, not detectable (detection limit 0.1 mg l⁻¹)

Table 2 Organic matter content in examined soil samples (%)

Sample	1	2	3	4	5	6	7
Depth (cm)							
0-2	8.5	–	23.8	11.1	5.2	6.0	9.0
2-20	8.2	10.7	7.5	10.5	8.7	5.9	8.5
20-30	7.7	10.7	7.9	9.8	8.8	5.8	6.6

3.1. Total Copper Concentration

The total copper concentration in the top 2 cm varies between regions, i.e., 180 mg kg⁻¹ in the Aleksandrovac sample (7), 166 mg kg⁻¹ in the Grocka 1 sample and approximately 100 mg kg⁻¹ in the samples from other regions (except sample 3). An average value for soils of the world has been reported as 30 mg kg⁻¹ [10]. The total copper concentration in background soils varies between 22.6 mg kg⁻¹ (Grocka) and 42.5 mg kg⁻¹ (Indjija). In the Grocka 3 sample the total concentration of copper is almost equal to the background level, because the soils are ploughed to 50 cm depth.

In some vineyards (samples 2, 5, 6 and 7) the total copper concentration in the upper 2 cm is generally lower than in the deeper samples, and the increase with increasing depth is

more gradual for samples 5 and 7. The increase of the total copper concentration with increasing depth in these samples probably results from its higher sand content, which is likely to mean higher permeability and increased copper mobility. However, the lower concentration at the surface results from no application of copper-based fungicides during the past 10 years in the Grocka 2 example (Fig. 3). The differences between vineyards could reflect different application rates, as well as different physical and chemical parameters in the soils but we do not have enough information to discern between possibilities.

The accumulation and distribution of total copper concentration in contaminated soils indicate that if total copper concentration is at an environmental threshold value, depth of contamination should be considered as a parameter in environmental regulations for soil quality, something that has not yet been attempted for heavy metal contamination in Serbia. Namely, the elevated copper concentrations observed at depths of 20 and 30 cm (samples 5 and 7), are 3-4.5 times higher than the regulatory limit (100 mg kg^{-1}) indicating significant soil pollution of deeper levels. There are a number of possible transport mechanisms, such as wind erosion and run off, as well as those related to flora (metal uptake, leaf and berry fall) and fauna (e.g. earthworms), in both horizontal and vertical directions, but discussion of these is beyond the scope of this paper. Also, the cultivation and the use of chemical amendments (e.g. fertilizers, pesticides, lime) on vineyard soils over the years are likely to be responsible for the physical and chemical soil properties and copper movement.

3.2. Plant Available Species

The plant availability of copper determined by EDTA extraction is high, with copper recovery rates being approximately twice as high for the contaminated soils (20% for sample 3 versus 43% for sample 6). The extractable contents usually increase with the total copper concentration. The Indjija sample (No 5) is an exception, where EDTA extractable amount of copper is not related to the total copper. The concentration of available copper detected in sample 2 (not treated with copper based fungicides last ten years) is about five times lower than total concentration, indicating that copper can remain possibly mobile for long periods of time.

Beside soil pH, the bioavailability of Cu may be influenced by organic matter. In the case of organic C, its relationship with Cu bioavailability may be indirect: the larger the organic C content, the larger the amount of bioavailable Cu. Organic matter is known to be responsible for a substantial retention of Cu in vineyard soils [3]. This positive relationship might also be due to decreased microbial activity in the most Cu-contaminated soils and to the consequent decrease in organic matter decomposition that would result in a build-up of organic C. However, in the examined soils from vineyards no significant effect of organic C is found considering either bioavailability (Fig 2.a) or extractability (Fig 2.b).

The NH_4OAc extractable contents are approximately two to twelve times lower than for the EDTA extractions. Differences between contaminated and uncontaminated soils are not observed. In the sample 2 this fraction is not detected since has probably been leached out. The concentrations of NH_4OAc copper detected in sample 3 are greater than those from some contaminated sites. Because this soil is ploughed to 50 cm depth, the soil from deeper levels with mobile, soluble copper is on the surface. The values obtained in the Indjija sample are in contrast to the amount of total copper found in these soils.

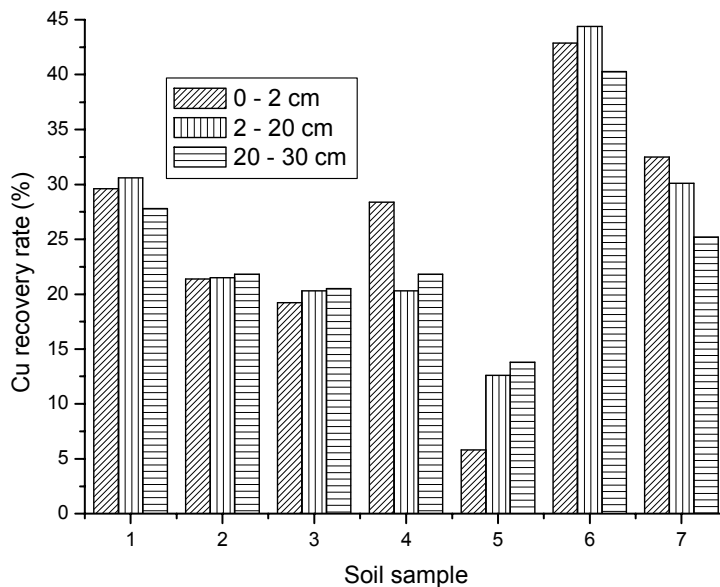


Fig. 2 (a) Assessment of the plant availability of copper by single-step extraction using EDTA as extractant

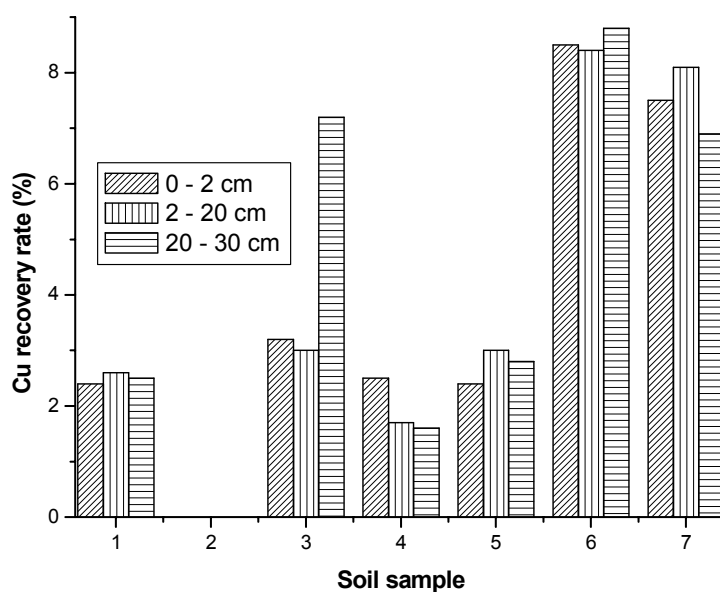


Fig. 2 (b) Assessment of the plant availability of copper by single-step extraction using NH₄OAc as extractant (in sample 2 was below the level of detection)

The results obtained suggest that the intensive use of copper sulphate in vineyard soils has caused an increase of Cu in soil leading to problems when crops other than hop or grapevine are grown. Normally, these two crops will not be affected, because their root systems are very deep. However, not only crops but also soil micro-organisms can be affected.

4. CONCLUSIONS

In summary, the most important results of these measurements are: there is a much higher portion of available copper in the vineyard soils relative to the background soils; there is no overall relationship between total and available copper in soils. This result indicates that the concentrations of active copper in soils cannot be predicted on the basis of total copper concentration, which is important for developing environmental guidelines.

In general, and for the purpose of predicting copper availability in soils (e.g., environmental, legislative purposes), total copper concentration should be regarded as important but not sufficient. The source of copper in soils, depth of contamination and soil properties need to be addressed for any prediction of copper availability in soils.

REFERENCES

1. Brun, L.A., Maillet, J., Richarte, J., Herrmann, P., and Rémy, J.-C.: Relations between extractable copper, soil properties and copper uptake by wild plants in vineyard soils, *Environ. Pollut.*, Vol. 102, pp. 151-161, 1998.
2. Besnard, E., Chenu, C. and Robert, M.: Influence of organic amendments on copper distribution among particle-size and density fractions in Champagne vineyard soils, *Environ. Pollut.*, Vol. 112, pp. 329-337, 2001.
3. Flores-Velez, L.M., Ducaroir, J., Jaunet, A.M., Robert, M.: Study of the distribution of copper in an acid sandy vineyard soil by three different methods. *Eur. J. Soil Sci.*, Vol. 47, pp. 523-532, 1996.
4. Karczewska, A.: Chemical speciation and fate of selected heavy metals in soils strongly polluted by copper smelters. In: Reuther, R. (Ed.), *Geochemical Approaches to Environmental Engineering of Metals*. Springer, New York, pp. 55-79, 1996.
5. McLaughlin, M.J., Hamon, R.E., McLaren, R.G., Speir, T.W., Rogers, S.L.: A bioavailability-based rationale for controlling metal and metalloid contamination of agricultural land in Australia and New Zealand. *Aust. J. Soil Res.*, Vol. 38, pp. 1037-1086, 2000.
6. Becket, P.H.T.: The use of extractants in studies on trace metals in soils, sewage sludges and sludge-treated soils, *Adv. in Soil Sci.* Vol. 9, pp. 143-179, 1989.
7. Radojević, M., Bashkin, N.V.: *Practical Environmental Analysis*. The Royal Society of Chemistry, Cambridge, 1999.
8. Brun, L.A., Maillet, J., Hinsinger, P., and Pépin, M.: Evaluations of copper bioavailability to plants in copper-contaminated vineyard soils, *Environ. Pollut.*, Vol. 111, pp. 293-302, 2001.
9. Pravilnik o dozvoljenim količinama opasnih i štetnih materija u zemljištu i vodi za navodnjavanje i metodama njihovog ispitivanja, Službeni glasnik Republike Srbije, br 23/94
10. Baker, D.E., Senft, J.P.: Copper. In: Alloway B.J., (Ed.), *Heavy metals in soils*, 2. London, Blackie Academic & Professional Press, pp. 179-205, 1995.

AKUMULACIJA I DOSTUPNOST BAKRA U ZEMLJIŠTIMA VINOGRADA U SRBIJI

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Pre više od sto godina uočeno je da su visoke koncentracije bakra toksične za mikroorganizme, tako da se CuSO_4 , kao glavni sastojak smeše poznate kao Bordovska čorba ($\text{Ca(OH)}_2 + \text{CuSO}_4$), još od 1882 godine koristi kao fungicid. Zbog dugotrajne upotrebe došlo je do akumulacije bakra u zemljištu. Prirodna koncentracija bakra u obradivom zemljištu je 5-30 mg kg^{-1} , dok površine koje su bile tretirane ovim fungicidom sadrže i do 1500 mg kg^{-1} .

U ovom radu prikazani su rezultati ispitivanja zemljišta iz vinograda koji su tretirani bakar-sulfatom. Uzorci su uzeti sa različitih lokacija u Srbiji. U ispitivanim uzorcima određena je ukupna koncentracija bakra izluživanjem sa carskom vodom. U cilju određivanja biodostupne i mobilne frakcije vršene su i tri pojedinačne ekstrakcije. Upotrebom bakar-sulfata došlo je do povećanja ukupne koncentracije bakra u zemljištu do 430 mg kg^{-1} . Uočene su znatne varijacije između pojedinih lokacija, ali je u 62% uzoraka koncentracija bila viša od 100 mg kg^{-1} , što je maksimalno dozvoljena koncentracija u poljoprivrednom zemljištu po nacionalnoj zakonskoj regulativi. Udeo bakra, dobijen pojedinačnim ekstrakcijama, izražen u odnosu na ukupnu koncentraciju, iznosio je 0,8-8,8% za amonijum-acetat i 5,8-44,4% za EDTA. Dobijeni rezultati pokazali su da bakar dugo ostaje mobilan u zemljištu, duže od deset godina, što može dovesti do njegovog izluživanja i migracije u dublje slojeve.

Ključne reči: bakar, akumulacija, dostupnost, zemljište vinograda