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Original Article

Geochemical Characteristics and Environmental Risks of Cu in the Soil of A Sloping Vineyard (Phu Tho Province, Vietnam)

Pham Thi Ha Nhung*, Tran Thi Thanh Huong, Dang Thi Nga, Nguyen Thanh Vinh, Nguyen Viet Truong, Nguyen Quoc Viet

VNU University of Science, 334 Nguyen Trai, Thanh Xuan, Hanoi, Vietnam

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Abstract: In the vineyards, the intensive use of cupric fungicides and fertilizers has resulted in Cu enrichment in the soils. Specifically, in sloping vineyards, the mobility of Cu can contribute to intensify the environmental risks. The research on geochemical characteristics of Cu is a key solution to explore the distribution of Cu in different geochemical fractions and understand the mobility and toxicity of this element in the environment. In this study, we aim to investigate the geochemical properties of Cu in the vineyard topsoil (0-20 cm) and subsoil (20-40-60 cm), using the improved three-step sequential extraction procedure developed by the Commission of the European Communities Bureau of Reference (BCR). In addition, the environmental risk is calculated by the environmental risk code (RAC) based on the percentage of Cu in the acid-soluble fraction. The results reveal that the mobility of Cu in the acid-soluble fraction (F1) and reducible fraction (Cu associated with the iron and manganese oxyhydroxides) (F2) tends to decrease with increasing soil depth. The major portion of Cu mostly exists in the strong bond with silicate clays (F4), accounting for 84% of total Cu content on average. Contrarily, the minor propotion of Cu associates with soil organic matter (F3) (3% on average). On the other hand, the content and proportion of Cu in the soil fractions are largely influenced by basic soil properties (organic matter contents and fine soil particles). In addition, under the impact of soil erosion, higher percentages of F1 and F2 fractions of Cu are observed in the surface soil layers at the top of the hill compared to those at the backslope of the hill. The mean calculated RAC of 10.66%, 5.76%, and 5.38% for the 0-20 cm, 20-40 cm, and 40-60 cm soil layers, respectively, demonstrate a low risk to medium environmental risk level in the studied vineyard. Although an overall low risk level is observed for Cu in the studied vineyard soil, the deposition of Cu originating from repeated Cu-based pesticides and erosion is of particular concern in the vineyard soils.

Keywords: Environmental risk, geochemical characteristics, sequential extraction, soil erosion, viticulture.

* Corresponding author.
E-mail address: phamthihanhung@hus.edu.vn

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1. Introduction

The accumulation of Cu in vineyard soils is probably not unexpected issue [1, 2] and a result of the repeated application of copper-based fungicides and fertilizers [3, 4]. In particular, in the sloping vineyard, soil erosion plays a key role in the transport of heavy metals such as Cu associated with eroded sediment particles [5, 6], then exert an impact on the environment and their geochemical phase distribution in the soils. However, the total Cu content is a poor predictor of the impact of contaminated soils and is insufficient for an adequate environmental risk assessment. Indeed, the Cu mobility, bioavailability, and toxicity to crops depend on its binding forms in the soil [7]. In addtion, this element can exhibit in different fractions strongly governed by soil components (such as organic matter; silt and clay particles; iron and aluminium oxides and oxy-hydroxides,…). Therefore, determining geochemical characteristics of Cu is appropriate to assess the lability of Cu in the soil. In addition, geochemical distribution of Cu significantly affects it behaviour in the soil with a particular regard to the oxic/anoxic conditions. Therefore, research on the binding forms of Cu by sequential extraction procedures may provide significant information to better apprehend the environmental risk caused by this element. Our previous study investigated the enrichment and bioavailability of Cu in the soil of a young steep vineyard in Phu Tho Province, NW Vietnam. Accordingly, three single extraction procedures and pseudo-total digestion were applied [3]. Meanwhile, in this study, we focus on the geochemical characteristics of Cu in the soil complemented with the environmental risk assessment by applying the sequential extraction method.

Sequential extraction procedurces have been used to fractionate the geochemical fractions of elements including Cu in solid samples (soil, sediments, sludge, solid waste,....) to assess the mobilization, retention, and bioavailability of these elements to plants and to groudwater [7-10]. In which, the Standards, Measurements and Testing Programme (SM&T, formerly BCR) of the European Commission has been widely applied in metal fractionation for soils and sediments [11]. However, the extraction procedures can exert an impact on the analytical results. Therefore, the improved BCR, a three-step sequential extraction procedure was designed by Rauret et al., [12]. This procedure provided an optimised method to determine the chemical forms of the soil-bound metals. Accordingly, metal ions in soils are partitioned between the different fractions, including the acid-soluble faction (metals bond to carbonates), the reducible fraction (metals bound to iron and manganese oxyhydroxides), the oxidisable fraction (metals bond to organic matter and sulfides), and the residual fraction (metals bond to phyllosilicate minerals). In which, the acid-soluble fraction of Cu as the most labile form easily released into the environment is widely considered in the environmental risk assessment [10]. The environmental risk code (RAC) based on the percentage of Cu in the acid-soluble fraction compared to the sum of all extracted forms of Cu is calculated as the environmental risk value of Cu [10, 13]. Therefore, the results are useful for obtaining information on potential mobility and transport of Cu in natural environments.

The specific goals of this research were: i) To determine the geochemical distribution of Cu in the topsoil (0-20 cm) and the subsoil (20-40-60 cm) in a young steep vineyard in Phu Tho Province, Vietnam; ii) To evaluate relationships between basic soil properties (soil pH, organic matter contents, major element (Mn, Fe, and Al), and soil texture) and the vertical distribution of Cu fractions in the studied vineyards; and iii) To assess the environmental risk of Cu.

2. Material and Methods

2.1. Study Area

This study area is a sloping vineyard planted in 2019, located in Thu Cuc commune, Tan Son district (a mountainous district) of Phu Tho

Province, northwest Vietnam. The soil in the vineyard is a Ferric Acrisols according to the World Reference Base for Soil Resources 2014 [14]. The mean slope of the studied plot is 10°, and the investigated slope section is of 38 m in length. The soil is well-drained and has slight erosion evidence at the backslope of the hill. Prior to planting a vineyard, there was long-term tea cultivation at the studied plot. However, the impact of tea cultivation was unobserved due to the completely removed and replaced former topsoils by tillage operations along the hillslope. Meanwhile, Melody Compact 49 WG has been used regularly in the vineyard at a typical dose of 1.5 kg/ha (in a solution equivalent to 600 l/ha) per application against downy mildew on grapevines since 2019. The treatment is repeated five times a year (in May, July, August, October, and December) during two harvest seasons. This fungicide uses two active ingredients to protect crops from fungal diseases, including copper oxychloride (406 g/kg) and iprovalicarb (84 g/kg) [3].

2.2. Soil Sampling

The topsoil (0-20 cm) and subsoil (> 20 cm soil layers: 20-40 cm and 40-60 cm) samples were collected in triplicate at two sampling locations at the middle of the backslope zone (profile A) and the center of the summit zone (profile B) of the hill in the vineyard using a hand auger. The soil samples were stored in clean polyethylene bags for transport to the laboratory.

2.3. Soil Analyses

The collected soil samples were air-dried at room temperature, disaggregated in a mortar with a pestle and then sieved to pass through a 2-mm sieve. Basic soil parameters such as pH, soil organic matter content (SOM), and particle-size distribution were determined following Vietnamese Standards (TCVN) and common methods. The pH was measured in deionized water with a soil/deionized water ratio of 1:2.5 using a digital pH meter (OHAUS starter 3100 pH) (TCVN 5979:2021). The SOM content was calculated by multiplying the soil organic carbon by the conversion factor of 1.74. The content of organic carbon in the soil was analyzed by the Walkley Black method, following H_2SO_4-aided oxidation of the organic matter with $K_2Cr_2O_7$. The excess $Cr_2O_7^{2-}$ is titrated with $FeSO_4.7H_2O$ using a Ferroin indicator (TCVN 8941:2011). The particle-size distribution was analyzed by the pipette method with 0.1 M sodium pyrophosphate (TCVN 8567:2010). All tests were performed in duplicate.

For determining the total contents of Cu and major elements (Mn, Fe, and Al), soil samples were ground to pass through a 250-µm sieve and dried at 105 °C in an oven for 24 hours. All sample containers (tubes, volumetric flasks, etc.) were acid-washed. The total contents of Cu, Mn, Fe, and Al were determined by the US EPA 3050B method [15] based on strong acid digestions with repeated additions of HNO_3 and H_2O_2, followed by additions of HCl to the initial digestate. Meanwhile, the three-step sequential extraction technique proposed by Rauret et al. [12] (the Community Bureau of Reference - BCR) was applied in evaluating the potential mobility and the geochemical distribution of Cu in the vineyard soil. Accordingly, the acid-soluble fraction of Cu was extracted using CH_3COOH (0.11 M) in the first step (F1). During the second extraction step (F2), Cu in the reducible fraction was released from iron and manganese oxyhydroxides by a fresh 0.5 M $HONH_2.HCl$ solution. In the third extraction step (F3), Cu bound to organic matter and sulfides (oxidisable fraction) was extracted by H_2O_2 (8.8 M) and CH_3COONH_4 (1.0 M) solutions. Copper in the residual fraction (F4) was determined by the US EPA 3050B method [15]. The contents of major element (Mn, Fe, and Al) and Cu in the different extracts were determined using the atomic absorption spectrophotometer. To validate the BCR sequential extraction, the sum of all extracted fractions (F1+F2+F3+F4) of BCR method and that of the total Cu content were compared using the following equation [16]:

$$Recovery\ (\%) = \frac{(\mathrm{F1 + F2 + F3 + F4})}{\mathrm{Total\ content}}\ x\ 100$$

In the present study, the mean recovery of 115% was obtained.

2.4. Environmental Risk Assessment

In order to assess the environmental risks of metals (including Cu) in different soil fractions, evaluating pollution by metals was performed by a risk assessment code (RAC) [10, 13].

Accordingly, the RAC was calculated as the percentage of Cu in the F1 fraction in the sum of all fractions (F1+F2+F3+F4). The classification of the RAC is described in 5 levels [17]: safe level (less than 1%), low risk level (1-10%), medium risk level (10-30%), high risk level (30-50%), and very high risk level (over 50%).

2.5. Statistical Analysis

The relationships between the vineyard soil characteristics and the geochemical fractions and total contents of Cu data were explored using the Pearson correlation test. The significance level was considered at $p < 0.05$ and $p < 0.01$. In addition, the one-way analysis of variance (ANOVA) was used to compare mean values between topsoil and subsoil properties at the significance level of $p < 0.05$. The statistical package used was SPSS version 20.

Table 1. Descriptive statistics (mean, min, max, and standard deviation) of basic soil parameters: $pH_{d.w.}$ (-), soil organic matter (SOM) contents (%), total Cu contents, major element contents, and soil particle sizes (%) determined in vineyard soil samples

	pH	SOM (%)	Cu (mg/kg)	Mn (mg/kg)	Fe (%)	Al_2O_3 (%)	Soil particle sizes (%)		
							Sand (2-0,05 mm)	Silt (0,05-0,002 mm)	Clay (<0,002 mm)
Topsoil (0-20 cm)									
Mean	5.27	1.84	42.78	154.02	3.61	9.03	37.01	43.34	19.65
Min	4.51	0.74	37.62	68.56	1.86	6.12	28.21	33.80	9.39
Max	7.06	2.57	49.86	286.93	4.63	10.96	48.61	52.80	33.79
SD	0.83	0.67	4.45	97.07	0.93	1.72	8.05	6.67	8.52
Subsoil (20-40-60 cm)									
Mean	5.82	1.66	34.58	167.39	5.30	8.84	36.01	46.40	17.59
Min	5.01	1.08	31.41	45.48	4.56	6.63	28.40	44.00	8.99
Max	6.62	2.31	37.84	286.82	6.21	9.94	43.01	48.20	27.60
SD	0.77	0.57	2.63	137.88	0.77	1.54	7.99	2.05	10.00

3. Results and Discussions

3.1. Soil Properties

The statistics of measured characteristics of the topsoil (0-20 cm) and subsoil (20-40-60 cm) in the studied vineyard such as pH, SOM, total Cu content, major element content (Mn, Fe, Al_2O_3), and particle size distribution (sand, silt, and clay contents) are presented in Table 1. Generally, the soil characteristics did not vary significantly between the topsoil and subsoil layers, except for the SOM and total Cu content. Vineyard soils in the studied plot are strongly acidic to neutral, with pH ranging from 4.51 to 7.06. The topsoil and subsoil displayed poor SOM contents (1.84 % and 1.66% on average, respectively). The soil particle size distribution showed that the soil texture is a sandy loam without any marked difference between the topsoil and the subsoil. According to the particle-size distribution, both topsoil and subsoil had loam textural characteristic with slightly higher clay content in the topsoil. The mean total Cu content in the topsoil (42.78 mg/kg) was higher than that in the subsoil (34.58

mg/kg), indicating an apparent enrichment of Cu in the topsoil. However, the Cu content was significantly lower than the pollution limit value of 150 mg/kg for soils figuring in Vietnamese standards (QCVN 03:2023/ BTNMT, 2023). The short-term applications of Cu-based fungicides in the studied vineyard can explain the slight Cu accumulation in the topsoil compared to the subsoil. Indeed, the Cu-fungicides have been applied for almost five years in the studied vineyard. Total Cu showed a significant positive relationship with SOM (R=0.88) (Table 2). This correlation revealed the important role of organic matter in Cu binding, especially the high molecular weight and insoluble fractions of organic matter [1-3].

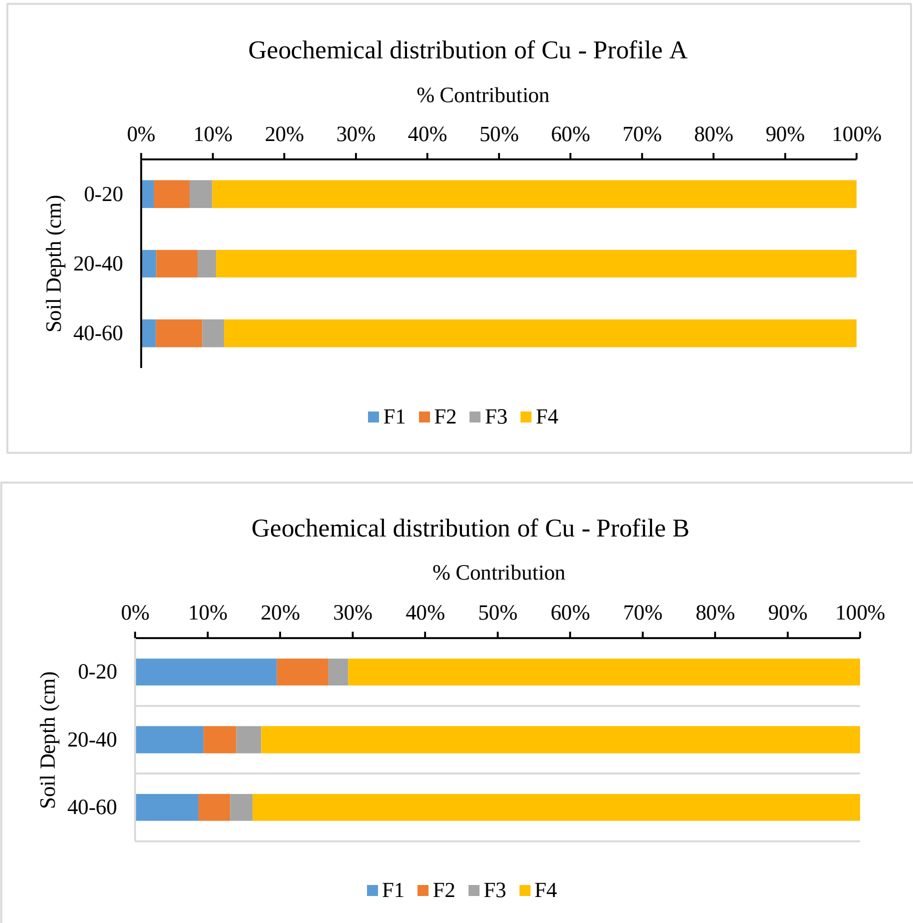

Figure 1. Contribution (%) of Cu in four extracted fractions in different soil sampling layers (F1: Acid-soluble fraction; F2: Reducible fraction; F3: Oxidisable fraction; F4: Residual fraction).

3.2. Geochemical Characteristics of Cu in the Vineyard Soil

The analytical results of the Cu fractionation observed by the improved three-step sequential BCR extraction procedure are presented in Fig. 1, in which the average percentage of each fraction is calculated in total Cu content (the sum of all fractions (F1+F2+F3+F4)). Generally, the proportion of the most mobile fraction (acid-soluble fraction) tended to decrease along the soil profile. Most of Cu was associated with the residual fraction of soils, accounting for 84% of total Cu content (on average). Conversely, the amounts of Cu exhibited in organic matter fraction were very low (3%, on average).

There was no significant difference between the proportions of extracted fractions of Cu in the topsoil and subsoil of the profile A (at the middle of the backslope of the hill), meanwhile, the higher percentages of F1 fraction of Cu was observed in the topsoil compared to the subsoil of the profile B (at the top of the hill). Moreover, the samples taken from the profile B displayed a remarkably high value of the proportion of Cu in the F1 fraction of compared to the soil samples of the profile A. This indicated the elevated environmental risk in low-energy zones within the landscape due to the strong mobility of Cu at the summit zone. These differences can be mainly explained by the impact of organic matter content and particle-size distribution. Since the higher contents of SOM and fine particles were observed in the soil samples collected at the backslope of the hill. Therefore, the Cu in the F4 and the F2 fractions fixed to silicate clays and bound to iron and manganese oxyhydroxides, respectively, can be explored. Accordingly, the contents and percentages of Cu in these two fractions were significantly higher in the soil of the profile A compared to the soil of profile B, especially in the topsoil (0-20 cm). In deed, in the sloping vineyard, the preferential association of Cu with the organic matter and fine-sized particles tended to transport downslope due to soil erosion [3]. As expected, in the present study, Cu in the F2 fraction was significantly correlated with total Fe and Al_2O_3 contents (R = 0.98 and R = 0.85, respectively). In addition, a positive correlation (R = 0.85) was also observed between Cu in the F4 fraction and silt content (Table 2). In contrast, Cu showed a less significant correlation with total Mn content in the studied soil.

Table 2. Correlation matrix between soil properties, total Cu, and geochemical fractions of Cu data

	pH	SOM	Mn	Fe	Al_2O_3	Sand	Silt	Clay	Cu-F1	Cu-F2	Cu-F3	Cu-F4	Cu-T
pH	1.00	-0.17	-0.94	0.36	0.01	0.85*	0.66	-0.92**	0.90*	0.42	0.79	0.21	0.24
SOM		1.00	0.29	0.15	0.56	-0.04	-0.42	0.17	0.09	0.17	-0.22	-0.40	0.88*
Mn			1.00	-0.05	0.33	-0.93**	-0.65	0.99**	-0.74	-0.10	-0.76	-0.14	-0.04
Fe				1.00	0.86*	-0.06	0.24	-0.03	0.64	0.98**	0.08	0.29	0.49
Al_2O_3					1.00	-0.33	-0.07	0.29	0.38	0.85*	-0.13	0.13	0.71
Sand						1.00	0.37	-0.95**	0.65	-0.04	0.60	-0.19	0.23
Silt							1.00	-0.63	0.67	0.39	0.73	0.85*	-0.19
Clay								1.00	-0.76	-0.10	-0.74	-0.11	-0.14
Cu-F1									1.00	0.71	0.63	0.34	0.50
Cu-F2										1.00	0.20	0.43	0.50
Cu-F3											1.00	0.44	0.02
Cu-F4												1.00	-0.31
Cu-T													1.00

SOM: Soil organic matter content; Cu-F1: Cu in acid-soluble fraction; Cu-F2: Cu in reducible fraction; Cu-F3: Cu in oxidisable fraction; Cu-F4: Cu in residual fraction; Cu-T: Total Cu;

*Significant at the level of $p < 0.05$; **Significant at the level of $p < 0.01$.

3.3. Environmental Risk Assessment of Cu in the Studied Vineyard Soil

Copper was bound to different soil fractions with the binding strength determining the bioavailability and the risk associated with its presence. In which, a proportion of Cu in the acid-soluble were the most toxic fraction and more available than Cu associated with the reducible, oxidizable and residual fractions [18]. Therefore, the risk assessment code (RAC) presented based on the percentage of Cu in the first fraction can be a useful tool to assess the mobility of Cu in the soil. In addition, the RAC was used as an environmental risk criteria for Cu that was found in the first extracted fraction in soil samples [10, 19].

In the studied vineyard, the codes as applied to the subsoil (20-40-60 cm) for Cu were less than 10% (Fig 2), implying a low risk level (RAC: 5.75% for 20-40 cm soil layer and 5.38% for 40-60 cm soil layer). Meanwhile, the calculated RAC showed that Cu (10.66%) in the F1 fraction of the topsoil layer (0-20 cm) can pose a medium risk to the environment. Although a low to medium risk was indicated for Cu, deposition of Cu-enriched soils originating from repeated application of copper-based fungicides and soil erosion is of particular concern in vineyards, in particular, in young steep vineyards with the intensive use of chemical fertilizers and fungicides.

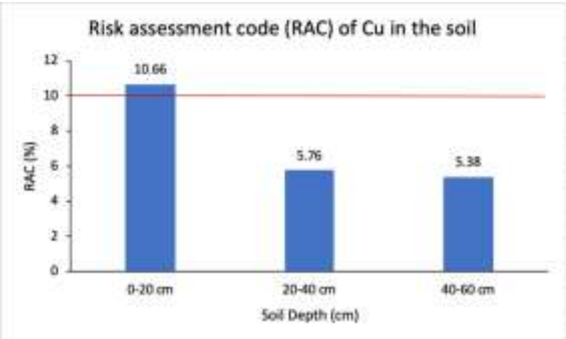

Figure 2. Average values of risk assessment code (RAC) (%) of Cu in the studied vineyard soil. The red line highlights RAC = 10%, above which a medium risk level is identified.

4. Conclusions

The BCR sequential extraction was applied to determine geochemical fractions of Cu in the vineyard soils (0-20 cm, 20-40 cm, and 40-60 cm soil layers) of a sloping vineyard in Phu Tho province, Vietnam. By studying the geochemical distribution of Cu in soils, the bioavailability and toxicity of this element can be ascertained. The results demonstrated that the geochemical characteristics of Cu in the soil were largerly influenced by soil erosion and soil properties (such as the significant positive relationship between soil organic matter content and total Cu (R=0.88); between total Fe, Al_2O_3 contents and Cu in the reducible fraction (R = 0.98 and R = 0.85, respectively); and between silt content and Cu in the residual fraction). A higher mean proportion of Cu in the acid-soluble fraction in the topsoil (0-20 cm) presented considerable environmental risk compared to that in the subsoil (20-40-60 cm). Accordingly, the risk assessment code (RAC) based on the percentage of Cu in the acid-soluble fraction showed a low (for subsoils) to medium (for topsoils) risk level of Cu in the studied vineyard soil. Hence, the high lability of Cu in the topsoil, which is expected to increase over time with the repeated use of Cu-based agrochemicals, can probably exert an environmental risk to the areas near the studied vineyard.

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