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Copper monitoring in vineyard soils of the Tikvesh region, North Macedonia

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Abstract

This research studies the copper contents in vineyard soils under vineyards affected by the long-term use of copper-based fungicides and evaluates the extent of this influence on the super accumulation in the main viniculture growing regions in North Macedonia. The soil samples were taken from individual vineyards located in the Tikvesh region, from two depths: 0-30 and 30-60 cm. At the same time, control samples were collected from each of the visited sites. The control samples were taken from untreated nearby locations under natural conditions in order to determine the background concentrations. The available copper (Cu) contents were analysed on soil samples taken from 100 locations, 50 of which represent vineyard soils (organic and conventional farming) and 50 control samples from nearby forests and sites. The main finding is that the average available copper concentrations are significantly higher in soils under vineyards, compared to the background concentration in control samples, especially in these with organic farming where the use of coper-based fungicides is more intensive. A comparison of the copper contents in vineyards to the background concentrations of control samples clearly confirmed the anthropogenic influence. A significantly very high level of copper (10.70-18.77 mg/kg) was measured in the soil samples from organic farming. The control samples contained a significantly lower concentration of copper, between average 1.39-1.62 mg/kg (0-30 cm) and 0.68-0.88 mg/kg (30-60 cm). According to the micronutrient rating as related to a soil test with the DTPA extraction reagent (Jones, 2001) applied in this study, a significant potential ecological risk has been noticed in the agricultural soil samples (organic and conventional production).

Key words: copper, soil, sample, vineyard, Tikvesh.

Introduction

Copper (Cu) is one of the heavy metals with greatest concern in the wine industry (Sun et al., 2016). Anthropogenic activities, such as mining, smelting, and the intensive use of pesticides and herbicides, are important copper (Cu) sources to the environment and may result with significant Cu accumulation in the soil (Smith 2009).

Copper was widely used in viticulture production for combating various types of fungal infection in agriculture, such as downy mildew and blackspot. Bordeaux mixture ($Ca(OH)_2 + CuSO_4$) has a traditional use as a protective agent, originally used in vineyards of France since 1885 and has been used for over a century. Numerous recent studies revealed that intensive and long-term application of these agents has negative effect on the environment because it leads to the contamination of soils with excessive quantities of copper (Komárek et al., 2010). Modern, commercial forms of copper fungicide have changed, but the active ingredient is still copper, due to which the accumulation of this element in soil is in the focus of interest in recent decades.

Copper rarely degrades or moves in through arable soil layers, which causes copper enrichment in vineyard soils (Pietrzak & McPhail, 2004). As a result, the long-term use of copper fungicides in viticulture has caused great copper accumulation in vineyard soils, resulting in negative effects on the environment through toxicity to aquatic and soil organisms (García-Esparza et al., 2006).

The European Community (EC) has fixed a maximum permitted field dose of copper at 6 kg/ha/year (Commission Regulation (EC) No 1410/2003) and maximum residue limits (MRLs) in vineyard soils, grapes and wine of 140 mg/kg (Council Directive 86/278/EEC), 20 mg/L and 1 mg/L (Commission Regulation (EC) No 1410/2003), respectively.

Vineyard soils have been found to contain 50–1500 mg/ kg of Cu, surpassing background values (5–30 mg/kg) by up to 300-fold (Chaignon et al., 2003). Mirlean et al. (2007) conducted a field study in southern Brazil and reported a maximum of 3200 mg/kg Cu in vineyard soils, which is several times higher than the EC regulation limit of 140 mg/kg. High Cu concentrations in soil can inhibit plant growth, generate reactive oxygen species (ROS), and produce disturbances in biochemical and physiological processes such as photosynthesis, enzyme activity, pigment synthesis, protein synthesis, and cell division (Mourato et al., 2009).

Important factors include certain soil properties that influence the bioavailability and toxicity of Cu (Rooney et al., 2006). Weng et al. (2005) reported a decrease in Cu toxicity with increasing soil pH. In addition, soil organic matter (SOM) and clay contents directly affect the extent of Cu damage in plants. Certain mineral elements present in the soil also affect the susceptibility of plants to Cu. For example, increases in available P may help precipitate heavy metals from the soil, thus decreasing the availability of metals to plants and other soil organisms (Cao et al., 2003).

Copper-based fungicides application doses and timing vary across regions depending on practices, regulation, hydroclimatic conditions, and vine variety. The European Union (Commission Implementing Regulation (EU) 2018/1981) recently decreased the maximal dose allowed from 6 to 4 kg Cu ha^{-1} $year^{-1}$ over seven years (Commission Implementing Regulation (EU) No 540/2011).

Researchers in this field (Schramel et al., 2000; Pietrzak & McPhail, 2004) indicate that determination of the total contents in the soil is insufficient for assessment, but it is necessary to determine its bioavailability, mobility, and toxicity. The most recent studies are directed towards development of different techniques to remediate soils loaded with copper. However, since the techniques of remediation are relatively expensive, time-consuming, and insufficiently effective, the optimal solution to this problem is a preventive measure that will restrict excessive intake of copper in the soil.

The aim of this study was to investigate the copper contents in vineyard soils in the Tikvesh Region of R. N. Macedonia, which is one of the most important wine regions in the country.

Material and methods

The study area and sampling method

The Tikvesh region is one of the biggest viticulture regions in the Republic of North Macedonia, located in the central part of the country along the Vardar River. The region encompasses several valleys surrounded by high mountainous frame in the south and south-west. Such relief conditions have a significant influence on the climate conditions in the region. The climate in the southern part is under the influence of a modified Mediterranean climate featuring long and hot summers, while the north of the region is under the influence of a continental climate with mild and wet winters. The mean annual air temperature is 13.3˚C, while the air temperature averages in the vegetation period (>5^0 C) are much higher and yield 18˚C, with summer maximums of over 40˚C. The precipitation sums in the vegetation period are very low and vary in the range of 300 to 500 mm. The favourable and harmonious climate coupled with dynamic soil and geographic convergence makes this region agro-ecologically suitable for growing many vine varieties with different periods of ripening.

Fig. 1. The Tikvesh wine district
(http://winesofmacedonia.mk/tikves-wine-district)

Within this monitoring, 50 samples, that contained different grape varieties, vine ages, and training systems were collected from 25 vineyards in 2022. All investigated vineyards were divided in two groups depending on the farming method:

- Organic vineyard production at 7 locations
- Conventional cultivation with the application of mineral fertilizers at total of 18 vineyards

The samples were collected using soil probes at two depths (0-30 and 30-60 cm). One composite sample has been prepared out of 10-20 subsamples, depending to the vineyard parcel size. Control samples were also collected from two depths, with harmonization of samples from one central location and 4 additional subsampling locations. In order to determine background concentration of Cu, control samples were collected from a nearby location under natural vegetation, which previously have never been cultivated. The total of 100 samples were collected, out of which 50 locations from vineyards and another 50 corresponding control samples.

The collected soil material (approx. 500gr soil) was packed, labelled, and transported to the accredited Laboratory for soil, fertilizer, and plant material at the Institute of Agriculture - Skopje, for further analysis of soil properties. Each of the sampling sites was geolocated by GPS and a corresponding GIS map indicating the exact locations was prepared in QuantumGis.

Soil analysis

In the preparatory phase in the laboratory, each soil sample was air-dried, lightly ground, and sieved through a 2 mm sieve. Standardized laboratory methods were used to test the basic chemical soil properties and quantities of available Cu:

- pH value - in 1:2.5 (v/v) suspension of soil in H_2O and 1 M KCl was determined using a glass electrode upon the MKC ISO method 10390:2015;
- free CaCO3 contents - by the volumetric method;
- organic matter contents - by the Tyurin method, modified by Simakov;
- easy available forms of phosphorus (P_2O_5) and potassium (K_2O) – by the AL method, according to Egner-Riehme
- available form of copper - by the DTPA method

Questionnaire Survey

Data for the past and current management practices were collected during the field visits by interviewing producers. For this purpose, a short questionnaire was developed for the following information:

- site description: size, regional location, date established, soil type, tillage, irrigation, use of chemical fertilizers, and organic manure, etc.;
- history of copper applications: past habits in copper applications, current application of copper or copper-based fungicides; the frequency, concentration, and type (i.e., commercial name, and chemical form) of copper spray application, if used at present.

Statistical analysis

Analysis of variance was performed using the SPSS 20.0 software.

Results and discussion

The sampling campaigns conducted during 2022 allowed us to perform an accurate analysis of Cu concentrations in the two soil depths of the researched vineyards and background concentration in natural conditions. The main soil characteristics are presented in Table 1 and 2.

According to the Macedonian Soil Information System, the soil cover is heterogenic, i.e., the vineyards in the studied area are mostly grown on Diluvial soils, Vertisols, Humic calcaric regosols, Regosols, and Aric regosols.

In agricultural soil, Cu availability is usually affected by several factors, such as soil pH and organic matter contents, since its availability is usually higher in acidic soil than in alkaline and organic matter (Keiblinger et al., 2018).

Soil pH is a factor that defines the “fertility” status, the level of which determines the availability of most essential plant nutrient elements as well as influences plant growth. With a change in pH, the concentration of some elements in the soil solution either increases or decreases (Jones, 2012). In the case of copper, soil reaction is reciprocal to its availability. With decreasing pH, the concentration of available Cu concentration is increasing, and vice versa. With regards to the soil reaction in water, all soil samples were characterized as alkaline, with pH varying from between slightly and moderately alkaline.

Laboratory soil tests revealed an exceptional low level of soil organic matter contents at the examined locations. The contents of organic matter showed a decreasing trend, from control samples with the highest average contents (3.20-3.29%) to the vineyards with conventional farming with the lowest (Table 2). The need to add additional quantities of organic matter in the form of manure, compost, or any other form of organic amendment, to either increase or maintain the soil organic matter contents, is considered as standard practice in viticulture production. In contrast, under intensive cultivation, organic matter level will continuously decline.

Copper concentration in vineyards soil fully depends on the quantity of its intake in the agroecosystem, which is related to vineyard age and number of treatments during a year (Ninkov et al., 2014). The average copper contents in researched soils are shown in Table 3.

Tab. 1. Soil properties from organic vineyards

Soil properties	pH				$CaCO_3$ (%)		Organic matter (%)		P_2O_5		K_2O	
	H_2O		KCl						mg/100g soil			
Depth (cm)	0-30	30-60	0-30	30-60	0-30	30-60	0-30	30-60	0-30	30-60	0-30	30-60
Min.	7.95	7.75	7.14	7.16	2.08	1.83	1.24	0.75	7.69	4.65	19.50	16.77
classification	*moderately alkaline*	*slightly alkaline*	*neutral*	*neutral*	*low*	*low*	*low*	*very low*	*low*	*very low*	*optimal*	*optimal*
Max.	8.43	8.43	7.63	7.72	27.45	29.95	4.36	2.78	14.92	9.30	38.99	34.31
classification	*moderately alkaline*	*moderately alkaline*	*alkaline*	*alkaline*	*high*	*high*	*medium*	*low*	*optimal*	*low*	*high*	*high*

*Classification according the working methods.

Tab. 2. Soil properties from conventional vineyards

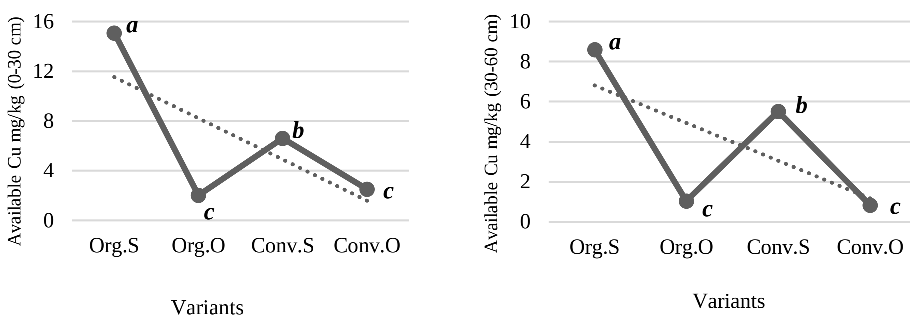
Soil properties	pH				$CaCO_3$ (%)		Organic matter (%)		P_2O_5		K_2O	
	H_2O		KCl						mg/100g soil			
Depth (cm)	0-30	30-60	0-30	30-60	0-30	30-60	0-30	30-60	0-30	30-60	0-30	30-60
Min.	7.74	7.71	7.00	7.00	2.50	2.65	0.82	0.14	6.33	4.66	16.53	14.99
classification	*slightly alkaline*	*slightly alkaline*	*neutral*	*neutral*	*low*	*low*	*very low*	*very low*	*low*	*very low*	*optimal*	*optimal*
Max.	8.32	8.31	7.62	7.52	36.60	37.43	4.34	3.50	91.59	45.36	54.47	36.01
classification	*moderately alkaline*	*moderately alkaline*	*alkaline*	*alkaline*	*high*	*high*	*medium*	*medium*	*very high*	*very high*	*very high*	*high*

*Classification according the working methods.

Tab. 3. Available copper contents in vineyard soils and relevant controls

Type of farming	Depth (cm)	Available Cu (mg/kg) 0-30	30-60
Organic	Control samples min-max	1.11-1.77	0.26-1.14
	*Classification	*medium-high*	*very low-medium*
	average±SD	1.39±0.22	0.68±0.33
	*Classification	*high*	*low*
	Vineyards sample min-max	3.86-18.77	2.33-10.70
	*Classification	*very high*	*high-very high*
	average±SD	12.09±6.13	5.67±3.57
	*Classification	*very high*	*very high*
Conventional	Control samples min-max	1.07-2.23	0.31-1.48
	*Classification	*medium-high*	*low-high*
	average±SD	1.62±0.39	0.88±0.30
	*Classification	*high*	*low*
	Vineyards sample min-max	2.51-23.80	1.21-10.10
	*Classification	*high-very high*	*medium-very high*
	average±SD	7.90±4.82	4.15±2.33
	*Classification	*very high*	*very high*

*Classification according to the micronutrient rating as related to a soil test with the DTPA extraction reagent.



Graph 1. and 2. Significance level of available Cu concentration in soil. Org.S (vineyard sample from organic farming), Org.O (control sample from organic farming), Conv.S (vineyard sample from conventional farming), Conv.O (control sample from conventional farming).
Note: different capital letters in the line indicate significant difference, at the probability level $P < 0.05$

Comparing the average available copper concentration with the corresponding control samples from every site, it can be concluded that the Cu contents are significantly higher in the soils cultivated with vineyards, (Table 3), especially when organic farming practices are applied.

The average copper contents in different vineyard soils and control samples (Table 3) have shown that soils at different depths had different copper contents. The results show that the surface soils (0-30 cm) contained the highest copper amount, while at the depth of 30 to 60 cm the copper concentrations were at a medium level.

Copper distribution in depths of the soil profile, primarily depends on the soil type, especially its specific physical and chemical properties. In most of the previous investigations, copper concentration was highest in the topsoil and rapidly decreased in the depth of soils under vineyards (Sun et al. 2018, Ninkov et al. 2014, Mirlean et al., 2007, Rusjan et al., 2006), which was confirmed in this study, as well. The process of copper relocation from topsoil into deeper layers was found to be very slow (Pietrzak & McPhail, 2004). Copper accumulates in the first several centimetres of the topsoil and is poorly mobile in the deeper soil horizons, since it firmly binds to organic soil components, carbonates, clay minerals and manganese, and iron oxides (Kabata - Pendias and Mukherjee, 2007).

Anthropogenic influence on vineyard soil contamination was evaluated by comparing the soil samples taken in the vineyards and the control sites. The comparison confirmed the expectation that due to prolonged historical copper applications, the concentrations of available copper in treated vineyards soil were significantly higher.

According to the micronutrient rating related to the soil tests with the DTPA extraction reagent (Jones, 2001), which was applied in this study, a significant potential ecological risk has been noticed in the agricultural soil samples (organic and conventional farming). The contamination factor has shown that most of the soil samples were moderately contaminated with Cu and some soil samples were considerably to strongly contaminated with Cu.

The data of copper concentration for all of the examined soil samples (Table 3) show that the highest individual sample value of 23.80 mg/kg was recorded in a vineyard with conventional farming.

According to the conducted field survey, high amounts of copper were applied on this site. However, high copper values might also be the result of long vineyard cultivation at this location, which implies the possibility of prolonged use of excessive amounts of copper-based formulations.

The average contents of available copper in the examined soil samples were estimated to a value of 12.09 mg/kg in the organic and 7.90 mg/kg in the conventional farming. These are similar to the concentrations found in other monitoring campaigns of copper contents in vineyard soils (Miotto et al., 2014, De Bernardi et al., 2022). Other authors, Farias et al., (2013), Ninkov et al. (2014), Ambrosini et al. (2018), and Fernandez-Calvino et al. (2008) identified significantly higher copper contents (> 20mg/kg) in their research of vineyard soils.

Overall, copper contamination of vineyard soils in the Tikvesh region appears to be lower than the levels reported in investigations in other countries. However, there are grounds for the need of monitoring soil copper levels more closely in all vineyards in the country, especially those grown for more than about 40 years. The current trend to use less copper is very welcomed from the point of view of soil management, but vigilance will still be required, even under low use regimes.

Analyses of basic soil properties (pH and organic matter contents) failed to show any significant relationships with the total soil copper concentration in the topsoils across the sampled vineyards. Given the geographical range of the study, with the attendant diversity of soil types represented in the sample, this was not unexpected.

Significantly very high level of copper measured in the organic vineyards (10.70-18.77 mg/kg) spatially and in the depth of the examined soils showed that the cupric treatments carried out over the years of cultivation have not scrupulously followed the laws regulating the Cu amount to be used in organic farming setting at 4 kg/ha/year (E.U Commission Work Programme 2018). Usually, the use of copper sulphate in organic farming takes advantage of the versatility of high doses and repeated applications without too much consideration for the environment. The high concentration of copper in deep soil, especially in the samples from farming soil indicated that copper could be transported to deeper soils, which might cause deep pollution, possibly even of groundwater, which was confirmed by Mirlean et al. (2007), also. Likewise, copper in the soil could transfer to grapes and then to wines (Vystavna et al., 2014).

Recently, the risk of heavy metals pollution in the environment has been increasing rapidly and creating turmoil, especially in the agricultural sector, by accumulating in the soil and in plant uptake (Tóth et al., 2016).

In the last decade, considerable work has been done to further reduce the minimal amount of copper needed for successful disease control in organic farming. However, the success of this work especially in wine growing was set back by the fact that the overall duration of the vegetation period in the past years has considerably increased due to climate change. Thus, a higher number of applications per year is needed so that the progress in reduction of the amount of copper per application was nearly completely counterbalanced by a higher number of applications.

Conclusion

The concentrations of available soil copper found in this investigation are consistent with patterns seen overseas, particularly as many of the vineyards in the study are old, above 10 years. The comparison confirmed the expectation that due to the prolonged historical copper applications, the concentrations of available copper in treated vineyards soil are significantly higher. A big number of older vineyards have very high soil levels of copper (above 2.5 mg/kg) requiring further investigation, especially in the field of copper content in the plants, which are grown in that soil. The copper concentration in the samples from the organic was significantly higher than in the samples from the conventional farming. A significantly very high level of copper measured in organic vineyards (10.70-18.77 mg/kg) spatially and in the depth of the examined soils has shown that the cupric treatments carried out over the years of cultivation have not scrupulously followed the laws regulating the Cu amount to be used in the organic farming.

In order to avoid contamination of viticulture soil with excessive copper concentrations, it may be necessary to reduce the number of applications, or, preferably, to stop the use of copper-based formulations. The concept of sustainable management of natural resources should consider the use of some formulations and ask whether the effects on the wider environment, particularly in the medium and long term, are an acceptable price to pay for crop protection.

The heavy metals contamination problem has become urgent, and needs radical and practical solutions to reduce the hazards as much as possible.

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Мониторинг садржаја бакра у земљишту винограда региона Тиквеш, Сјеверна Македонија

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Сажетак

Циљ истраживања је да се испита садржај бакра у земљиштима винограда погођеним дуготрајном употребом фунгицида на бази бакра и процијени степен обим утицаја тог третирања на суперакумулацију бакра у главним виноградарским регијама у Сјеверној Македонији. Узорци земљишта узети су из винограда који се налазе у регији Тиквеш, с двије дубине: 0-30 и 30-60 cm. Истовремено су прикупљени и контролни узорци са сваког од посјећених мјеста. Контролни узорци узети су с нетретираних оближњих локација у природним условима како би се одредиле природне концентрације бакра у земљишту. Садржај бакра (Cu) анализиран је на узорцима земљишта узетим са 100 локација, од којих је 50 потицало из винограда (еколошки и конвенционални узгој), а 50 контролних узорака из оближњих шума и локалитета. Главни налаз је да су просјечне расположиве концентрације бакра знатно веће у земљишту под виноградима, у поређењу с природном концентрацијом бакра у контролним узорцима, посебнп у оним с еколошким узгојем гдје је употреба фунгицида на бази бакра интензивнија. Поређењем садржаја бакра у земљишту винограда с природним концентрацијама контролних узорака јасно је потврђен антропогени утицај. У узорцима земљишта из еколошког узгоја измјерен је статистички врло значајан висок ниво бакра (10,70-18,77 mg/kg). Контролни узорци садржали су значајно нижу концентрацију бакра, између просјечних 1,39-1,62 mg/kg (0-30 cm) и 0,68-0,88 mg/kg (30-60 cm). Према оцјени микронутријената у односу на испитивање тла с ДТПА екстракцијским реагенсом (Jones, 2001.) примијењеним у овој студији, уочен је значајан потенцијални еколошки ризик у узорцима пољопривредног земљишта (еколошка и конвенционална производња).

Кључне ријечи: бакар, земљиште, узорак, виноград, Тиквеш.

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