Copper in Surface Layer of Vineyard Soils on Island Hvar

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Summary

The frequent use of copper fungicides in grape production results in increased accumulation of total copper in the surface layer of vineyard soils. The objective of this research was to survey copper concentration and determine degree of pollution or contamination with copper in surface soils of vineyards on island Hvar. Sampling was undertaken on anthropogenic colluvial soils, anthropogenic terrace soils on pleistocene calcareous aeolian sands and anthropogenic soils on quaternary alluvial, aeolian and diluvium depositions. Concentrations of total copper in the vineyard soils under research range from 50.60- 276.33 mg kg^{-1}. Copper concentrations were significantly ($p<0.01$) higher in anthropogenic soils on quaternary alluvial, aeolian and diluvium depositions than on other soils sites tested. According to the specifications provided within the "Regulations on Protection of Cultivated Land from Contamination by Hazardous Substances" (NN 9/14) sixteen out of twenty-seven vineyard soils under research were polluted and five were contaminated with copper. The results of this research provide further data relevant to the inventory of heavy metals in vineyard soils of this part of the Croatia.

Key words

copper, accumulation, vineyard soil, anthropogenic soil

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Introduction

In recent years content of heavy metals in the soil caused by human activities have gradually increased, resulting in the deterioration of the environment. Agricultural soil contamination with heavy metals through the repeated use of chemical fertilizers and pesticides is one of the most severe ecological problems. Heavy metals are the main pollutants that accumulate in vineyards soils. Because of viticulture intensive practice, the phytopharmaceuticals and fertilizers are the main source of metal pollution. Intensive and long term use of copper based fungicides has increased soil copper concentrations and this is likely most pronounced in vineyards (Komarek et al., 2010). The frequent use of copper based fungicides has resulted in copper accumulations in surface layer of vineyard soils far in excess of trace amounts that are required for healthy plant growth. Numerous studies have indicated that prolonged use of copper based chemicals often results in soil contamination (Besnard et al., 2001; Flores-Velez et al., 1996). Copper based fungicides have been in use with wine-growing as a plant protection product against fungal diseases *(Plasmopara viticola* (B. and C.) Berl. and De Toni and *Phomopsis viticola* (Sacc.) Sacc) since the 18th century. In Croatia, mostly used copper based fungicides against fungal diseases in wine-growing are: copper sulphate, copper (I) oxide, copper oxichloride, copper hydroxide, copper-hydroxide-potassium sulphate complex, copper-hydroxide-Ca-chloride complex, combinations of copper and organic fungicides, and combinations of copper and mineral oils (Vitanović, 2012). The number of annual treatments with copper fungicides is estimated to be extremely high, 8-14 (Gračanin, 1947; Flores Velez, 1996; Romić et al., 2001). Depending on its concentration in soil copper can be a toxic element and micronutrient. From the eco-toxicological point of view, high copper concentrations may alter cellular division in some plants (Arduini et al. 1994), affect the activity and diversity of soil microorganisms (Díaz-Raviña et al. 2007; Fernández-Calviño et al. 2010), and cause damage in the detritivorous populations (Paoletti et al. 1998; Daoust et al. 2006). Copper in soil is bound to soil organic matter, adsorbed to clay surface, bound to Fe and Mn oxides, in the matrix of primary silicate minerals, in secondary minerals or within amorphous matter (Chaignon et al., 2002). The sum of all above is defined as total copper in soil. The total copper content in soils is a useful indicator of soil contamination. According to Vitanović et al. (2012) application of copper fungicides to vineyards of coastal Croatia has resulted in the accumulation of copper residues in surface soils and an average of 2.90 to 4.20 kg/ha of copper is introduced into vineyards each vegetative year through treatment of the vine with copper fungicides. In this study, we undertook a survey of total copper concentrations in vineyards soils of island Hvar and determined which soil type accumulated the most copper. According to the regulations (NN 9/14) and obtained results, the vineyard soils under research are defined as either contaminated or polluted with copper.

Materials and methods

Selection of locations

For this research we selected vineyard soils on island of Hvar (Figure 1). The island of Hvar belongs to the group of Central Dalmatian islands and according to the Regulations of geographical areas of wine growing (NN 74/12) belongs to the Middle and South Dalmatia wine region. Following an extensive analysis of the area, three different locations, which differ in geology, were selected for the research. Areas with anthropogenic colluvial soils developed on quaternary colluvium depositions were selected as location A (N 43°07', E 16°39'). Location B was comprised of areas with anthropogenic terrace soils on pleistocene calcareous aeolian sands (N 43°08', E 16°40'), while areas with anthropogenic soils on quaternary alluvial, aeolian and diluvium depositions were selected for location C (N 43°10', E 16°37'). Nine vineyards were selected from each of the locations. The age of the vineyards had an important role in the selection, because of long-term use of copper fungicides. Each of the selected vineyards is more than 40 years old. Sizes of vineyards are in range 200-800 m^2.

Figure 1. Locations of vineyards on island Hvar

Soil sampling

Soil sampling was carried out in all locations in each of the nine vineyards. Samples were taken by a 30 mm diameter cylindrical probe from 0 - 0.3 m. In each vineyard 10 single samples were taken and homogenized to obtain one composite sample. Samples were air-dried, passed through 2 mm sieve and stored in plastic boxes at room temperature.

Soil analysis

In the prepared samples the following parameters were determined: pH, active lime, total carbonates and humus. Soil reaction (pH) was determined potentiometrically with a glass electrode in water and 1 M KCl in soil:water suspension with 1:2.5 ratio (w/v), active lime by the Druines-Galet method, total carbonates by the Scheibler calcimeter and humus by Tjurin method. All methods of soil chemical analyses are described in Priručnik za pedološka istraživanja (Škorić, 1982). Total copper in the surface layer (0 - 0.3 m) was evaluated after digestion with aqua regia (ISO 11466, 2004). Three g of soil (previously prepared and crushed to dust) was measured in a 250 ml reaction flask and 0.5-1 ml of double-distilled water, drop by drop, 21 ml of 12.0 M hydrochloric acid and 7 ml of 15.8 M nitric acid were added. The prepared mixture was left at room temperature for 16 h to allow oxidation of organic components within it. After settling, the content above the sediment was filtered through filter paper (8 μm pore width, 150 mm diameter) into a 100-ml volumetric flask. The sediment from the filter paper was carefully washed with diluted nitric acid. The flask was filled with double-distilled water up to the mark, and total copper was measured in such prepared sample. Total copper content in soil was determined by flame atomic absorption spectrometry (Varian 220, 2004). Texture was determined by sieving and sedimentation method (ISO 11277, 2004). Classification of soils by texture was according to the U.S. system (Soil Survey Manual, 1951).

Statistical data analysis

All indicators were processed by analysis of variance (ANOVA) and means were compered using Tukey test at $p<0.01$. The software used for this purpose was Statview (SAS, Version 5.0).

Results

Soil chemical and physical properties

The results of chemical and physical analyses of anthropogenic colluvial soils (A) are presented in Table 1. Silt loam texture dominates in these soils. The soils are skeletal, very deep, their water capacity is low, while the air capacity is high. They have very high carbonate content (21.10-58.17%).

Anthropogenic terrace soils on pleistocene calcareous aeolian sands (B) have very high carbonate content (52.69-86.90%), low humus content (0.80-1.19%) and sandy loam texture (Table 2). Their water capacity is very low, while the air capacity is very high.

Variations of the properties of anthropogenic soils on quaternary alluvial, aeolian and diluvium depositions (C) are a result of the complexity and heterogeneity of parent material. There was a great variability (Table 3) in the mechanical composition (loam-clay loam), pH value (6.06-7.96) and carbonate content (1.90-9.80%).

Table 4 shows concentration of total copper in surface layer of researched soils. The average copper value for the 27 samples

Table 1. Chemical and physical properties of anthropogenic colluvial soils (A)

Vineyard	pH		Total carbonates	Active lime	Humus	Clay	Silt	Sand	Texture type
	H_2O	KCl	%	%	%	%	%	%	
A 1	8.32	7.48	21.57	6.15	5.02	15.31	58.91	25.78	silt loam
A 2	8.34	7.56	22.53	6.16	3.81	15.13	57.01	27.86	silt loam
A 3	8.26	7.37	21.10	7.37	4.09	14.71	59.06	26.23	silt loam
A 4	8.34	7.61	38.40	7.17	4.63	12.16	66.78	21.06	silt loam
A 5	8.23	7.54	31.80	6.38	4.95	12.73	55.60	31.67	silt loam
A 6	8.2	7.39	40.13	6.78	5.38	12.98	54.57	32.45	silt loam
A 7	8.53	7.61	58.17	11.18	2.57	10.10	49.96	39.94	silt loam
A 8	8.39	8.39	53.86	10.89	3.38	10.24	51.32	38.44	silt loam
A 9	8.51	8.51	50.39	9.41	2.52	10.58	50.09	39.33	silt loam
s	0.11	0.42	14.35	2.01	1.05	2.07	5.37	6.75	

s-standard deviation

Table 2. Chemical and physical properties of anthropogenic terrace soils (B)

Vineyard	pH		Total carbonates	Active lime	Humus	Clay	Silt	Sand	Texture type
	H_2O	KCl	%	%	%	%	%	%	
B 1	8.19	7.68	52.69	2.40	1.19	6.25	34.52	59.23	sandy loam
B 2	8.19	7.68	54.61	2.42	0.91	5.83	32.94	61.23	sandy loam
B 3	8.21	7.69	54.67	2.55	0.84	5.97	34.51	59.52	sandy loam
B 4	8.47	7.73	63.82	2.07	0.80	4.65	30.65	64.70	sandy loam
B 5	8.52	7.85	58.85	2.07	0.97	4.23	29.94	65.83	sandy loam
B 6	8.49	7.87	59.61	2.03	0.81	4.13	26.29	69.78	sandy loam
B 7	8.57	7.89	86.90	1.82	0.79	3.93	28.29	67.78	sandy loam
B 8	8.59	7.77	85.71	1.97	0.95	3.37	26.24	70.39	sandy loam
B 9	8.61	7.81	86.68	1.92	0.95	3.37	25.77	70.86	sandy loam
s	0.18	0.08	14.89	0.25	0.13	1.11	3.51	4.61	

s - standard deviation

Table 3. Chemical and physical properties of anthropogenic soils on quaternary alluvial, aeolian and diluvium depositions (C)

Vineyard	pH		Total carbonates	Active lime	Humus	Clay	Silt	Sand	Texture type
	H_2O	KCl	%	%	%	%	%	%	
C 1	6.06	5.23	2.10	0.20	1.45	18.23	39.43	42.34	loam
C 2	6.20	5.37	1.90	0.20	1.74	17.56	36.20	46.24	loam
C 3	6.29	5.76	2.33	0.20	1.56	18.64	36.91	44.45	loam
C 4	7.53	6.74	2.43	0.20	1.91	24.78	44.99	30.23	loam
C 5	7.37	6.63	2.30	0.20	2.63	25.68	43.09	31.23	loam
C 6	7.45	6.45	2.37	0.20	2.62	23.97	43.58	32.45	loam
C 7	7.92	7.23	8.63	0.33	2.20	39.26	36.51	24.23	clay loam
C 8	7.96	7.25	9.80	0.63	1.23	38.26	38.59	23.15	clay loam
C 9	7.89	7.20	9.10	0.63	2.45	39.13	36.67	24.20	clay loam
s	0.78	0.79	3.49	0.19	0.52	9.19	3.45	9.05	

s - standard deviation

Table 4. Total copper concentration (mg Cu kg^{-1}) in surface layer (0-0.3 m) of researched soils

Vineyard	Location A	Location B	Location C
		mg Cu kg^{-1}	
1	129.33	73.47	103.00
2	99.07	89.43	115.00
3	106.67	50.60	122.00
4	75.37	61.77	130.67
5	93.17	87.90	221.67
6	86.33	71.97	137.67
7	55.43	62.87	276.33
8	55.67	72.63	132.67
9	53.50	69.13	179.33
Average	83.84a	71.09a	157.59b

A - anthropogenic colluvial soils on quaternary colluvium depositions;
B - anthropogenic terrace soils on pleistocene calcareous aeolian sands;
C - anthropogenic soils on quaternary alluvial, aeolian and diluvium depositions. Different letters in the table indicate means differing significantly according to Tukey test at P<0.01

examined was 129.33 mg kg $^{-1}$ (range 50.6-276.33 mg kg $^{-1}$). The total copper concentrations in anthropogenic colluvial soils ranged between 53.50- 129.33 mg Cu kg^{-1}. Anthropogenic soils on pleistocene calcareous aeolian sands contained 50.60-89.40 mg Cu kg^{-1} and anthropogenic soils on quaternary alluvial, aeolian and diluvium depositions contained 103-276.33 mg Cu kg $^{-1}$. The highest concentration of total copper was recorded in anthropogenic soil on quaternary alluvial, aeolian and diluvium depositions from the vineyard C7 (276.33 mg Cu kg^{-1}). It is also type of soil with the highest average concentration of total Cu in all soils covered by the research.

Discussion

Vineyard soils of island Hvar contained from 50.60 to 276.33 mg Cu kg^{-1}. These levels are clearly higher than those corresponding to surface horizons of other cultivated soils. Arable soils usually contain 5-30 mg Cu kg^{-1}, while concentrations of total copper in treated vineyards can range between 100 and 1500 mg Cu kg^{-1} (Besnard et al., 2001). These results are similar to results obtained by research in Croatia. Romić et al. (2001) declared that vineyard soils of continental Croatia contained from 30 to 700 mg Cu kg^{-1}. Vitanović et al. (2010) reported that copper concentration in surface soils of vineyards in coastal Croatia are in range from 70.50 to 625.79 mg kg^{-1}. Jurisić et al. (2012) found total copper concentration up to 394 mg kg^{-1} in vineyard soils in north-west part of Croatia. Copper concentrations above 100 mg kg^{-1} have been also found in other countries with tradition in vineyard production (Chaignon et al., 2002; Magalhaes et al., 1985; Ramos. 2006; Rusjan et al., 2007; Vavoulidou et al., 2005). In Croatia, total copper maximal allowable concentrations (MAC) of up to 120 mg kg^{-1} are allowed in agricultural soils (NN 9/2014). MAC of copper in agricultural soils depends on soil texture and humus content of soil. For clayey soil MAC of copper is 60 mg kg^{-1}, for loamy soil is 90 mg kg^{-1} and for sandy soil is 120 mg kg^{-1}. In clayey soil, if humus content is lower than 3% MAC for loamy soil is used. In case of loamy soil MAC for sandy soil is used when humus content is lower than 3%. This classification is determined by comparison of actual pollution with MAC of pollution or by the degree of pollution (So=content in soil – mg kg^{-1}/ maximal allowable concentrations). Based on this, soils are grouped into five classes: pure soil (So<0.25), increased soil pollution (So 0.25-0.50), high soil pollution (So 0.50-1.00), polluted soil (So 1.00-2.00) and contaminated soil (So>2.00). Twenty-one out of twenty-seven vineyard soils under research deviate from the maximum allowed copper concentrations. Sixteen vineyards were polluted and five vineyards (C3, C4, C5, C6 and C7) in research were contaminated with copper. The analysis of variance of total copper concentrations (D=73.89* > LSD 0.01 = 48.74) indicates a considerable difference in total copper concentrations (with 99% certainty) between colluvial anthropogenic soils and anthropogenic terrace soils on quaternary alluvial, aeolian and diluvium depositions. There is also considerable difference (D=86.56* > LSD 0.01 = 48.74) in total copper concentrations (with 99% certainty) between colluvial anthropogenic soils and anthropogenic terrace soils on pleistocene calcareous aeolian sands. Significantly higher concentrations of copper were identified in anthropogenic soils on quaternary alluvial, aeolian and diluvium depositions. These soils have loam and clay loam texture. They are heavier than other soils in research. Stronger bond of copper with clay particles can be the reason for higher concentrations of total copper in heavier soils (Lagomarsino et al., 2010). In lighter soils copper is leaching into lower layers more excessive and faster (Vitanović., 2012). Other reason for higher copper concentrations is location of vineyards. Vineyards are located on flat terrain in the area that is exposed to more severe disease attacks and consequently use of copper based fungicides on these type of terrain are more frequent (Pellegrini et al., 2010).

Conclusion

This research showed that application of copper fungicides in vineyards of island Hvar has resulted in the accumulation of copper residues in surface soils. Concentrations up to 276.33 mg Cu kg^{-1} were found in anthropogenic soil on quaternary alluvial, aeolian and diluvium depositions. Anthropogenic soil on quaternary alluvial, aeolian and diluvium depositions contain significantly (p<0.01) higher concentrations of total copper compared to other soils under research. Sixteen out of twenty-seven vineyards under research were polluted and five were contaminated with copper. Special attention should be taken in organic vineyard production because in this type of production some copper based fungicides are allowed. The results of this research provide further input towards the inventory of heavy metals in vineyard soils of Croatia.

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