Copper, iron and zinc in surface layer of Primošten vineyard soils

Concentration en cuivre, fer et zinc dans la couche supérieure du sol de vignobles de la région de Primosten

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Summary

Long-term use of copper fungicides causes increased accumulation of total copper in the surface layer of vineyard soils. Many of authors has researched the anthropogenic influx of copper in such soils, which can result in environmental risks. The research revealed that vineyard soils contain 288.52 mg/kg of copper, 102.20 mg/kg of zinc, and 28.86 g/kg of iron on average. Considering the average concentrations of the metals under research, all soils under research are highly contaminated with zinc (So=0.50), and polluted with copper (So=4.76), according to Bašić (1994). Each of the vineyard soils under research is contaminated with copper, according to the "By-laws on Protection of Cultivated Land from Contamination by Hazardous Substances" (National Gazette No. 15/1992). There is a significant difference in concentrations of total copper between the vineyard and forest soils based on the variant analyses results (F_{exp} = 5.60*). The research results indicate that copper and zinc are fully correlated. 94.09% of the total copper variation occurred due to a modified concentration of total zinc in the soil, while the remaining 5.91% was caused by some other factors. According to the same results, copper and iron are very weakly negatively correlated. 1.7% of the total copper variation occurred due to a modified concentration of total iron in the soil, while the remaining 98.3% was caused by some other factors. The results are a contribution to the inventory of heavy metals in vineyards.

Key words: heavy metals, copper, iron, zinc, vineyard (anthropogenic) soils.

Introduction

Contamination of soil with heavy metals is a central and current issue in modern ecology, particularly agroecology. Heavy metals are the basic indicator of contamination, both of soil and groundwater, although frequently in trace amounts only. Agricultural soils are particularly exposed to excessive contamination by heavy metals, the reasons being industrial and heating plants, traffic, households and anthropogenic impact. The anthropogenic impact is especially conspicuous in vineyard soils, orchards and private plots. The researches had the following objectives: to identify concentrations of total copper, zinc and iron in the surface layer of wine-growing soils in the Primošten vineyards and to determine their possible correlation. Copper fungicides have been in use in wine-growing as plant-protection products against fungal diseases since the 18th century (Lafforgue, 1928). Bordeaux mixture (copper sulfate) is one of the oldest fungicides, which has been in use in wine-growing for many years; however, numerous other copper-based preparations are also used in Croatia nowadays. According to information gathered to date, long-term use of copper fungicides in wine-growing results in influx of significant quantities of copper, which remain in the surface soil layer at 0-15 cm, which has been confirmed by a number of researches (Gračanin, 1947; Drouineau and Mazoyer, 1962; Delas, 1963; Geoffrion, 1975; Li, 1994; Deluisa et al., 1996; Flores Velez, 1996; Romić Marija and Romić D., 1998; Narimanidze and Bruckner, 1999; Romić Marija et al., 2001; Brun et al., 2003). Since total copper has competition in the soil in acquisition of nutrients through plant roots, and because better yield depends on their very relations (Anić, 1973; Vukadinović and Lončarić, 1998), concentrations of total zinc and iron were also under research. Since such researches had not been carried out in Dalmatia yet, and considering the fact that 2-5 kg of Cu/ha is introduced into vineyard soils each vegetative year, we thought it would be interesting to carry out researches in the Primošten vineyard area. Namely, the high number of sprayings in this vineyard area is conditioned by a micro-climate favorable for development of vine diseases, as well as traditional methods used in cultivation and protection.

Material and Methods

The Primošten vineyards are distinguished for cultivation of one of the most significant Croatian wine varieties, Babić, which is the basis for production of top-quality wine. For reasons of their attractiveness (nominated for UNESCO's World Heritage list), vineyards of the Bucavac wine-growing location (N 43°56', E 16°94') were selected for the research. Sampling was made on characteristic anthropogenic soils of terraces on cretaceous limestones, in five representative vineyards A1-5, at altitudes ranging from 16 to 35 m, as well as in three test areas Ak1-Ak3 (N 43°57', E 15°94'), at altitudes ranging from 18 to 30 m. Forest soils which had never been exposed to application of copper-based plant-protection products were selected to serve as test areas in order to determine the so-called background concentration. Average samples were taken by a 30 mm dia cylindrical probe at two depths, from 0 to 20 cm and from 20 to 40 cm (Brun et al., 2001), upon which physical and chemical analyses were made. The following chemical properties were determined: soil reaction – pH value (potentiometrically with glass electrode in water and KCl), active lime (Druines-Galet method), total carbonates (Scheibler calcimeter), humus content (permanganate method acc. to Kotzmann), exchangeable potassium content (extraction with 1M ammonium acetate), phosphorus content (acc. to Troug) (Škorić, 1982). Total copper, iron and zinc content were determined, only at surface layer (0-20 cm), by atomic absorption spectrophotometry with flame (Varian 220). The following physical analyses were performed: identification of skeleton (acc. to Gračanin) and of mechanical composition of soil (with Na-pyrophosphate). In addition, the ten-question survey was used, with the purpose of acquiring data on: vineyards (soil, age), agrotechnical measures applied and plant-protection products in use. The core element comprised all wine-growers in whose vineyards sampling of soil under research was made. All indicators were processed by the statistical method of variant analysis (ANOVA). The software used for this purpose was STATVIEW (SAS, Version 5.0).

Results and Discussion

Results of the chemical analyses indicate that the anthropogenic soils of terraces on cretaceous limestones are very humous and with alkali reaction growing with their depth. The soils have a low content of total carbonates and active lime, and are very rich with nitrogen and pretty much supplied with potassium and phosphorus (content growing with depth), as opposed to the soils in test areas, which are rather carbonate and limey, as well as rich with nitrogen, well-supplied with potassium, but very poorly provided with phosphorus (Table 1).

vineyard / test area	depth cm	pH		total carbonates	active lime	humus	N	K_2O	P_2O_5
		H_2O	nKCl	%			‰	mg/100g	
A1	0-20	7.82	7.06	1.2	0.00	3.50	1.75	101.2	80.9
A1	20-40	7.95	7.06	1.6	0.00	5.90	2.95	71.4	30.2
A2	0-20	7.51	6.86	1.2	0.00	8.88	4.44	363.8	254.2
A2	20-40	7.54	6.77	1.2	0.00	10.20	5.10	271.9	94.7
A3	0-20	7.79	7.08	4.1	0.00	8.03	4.01	84.8	107.8
A3	20-40	7.97	7.08	4.1	0.00	8.51	4.25	96.9	106.0
A4	0-20	8.00	7.18	9.9	0.69	10.07	5.03	57.1	22.4
A4	20-40	8.05	7.15	9.9	1.97	5.62	2.81	47.7	12.8
A5	0-20	8.18	7.18	2.9	0.00	5.30	2.65	62.1	29.2
A5	20-40	8.20	7.29	2.1	0.00	5.33	2.66	42.2	11.9
Ak1	0-20	7.80	7.03	40.9	9.11	9.66	4.83	48.8	9.1
Ak1	20-40	8.00	7.25	48.0	8.48	5.86	2.93	44.4	4.5
Ak2	0-20	7.97	7.22	35.9	16.25	11.24	5.62	62.7	6.9
Ak2	20-40	8.13	7.23	47.0	18.64	8.49	4.24	50.0	7.9
Ak3	0-20	7.90	7.11	47.0	22.72	7.68	3.84	27.9	2.1
Ak3	20-40	8.39	7.18	41.3	25.56	3.52	1.76	15.8	5.1

Table 1 Chemical properties of anthropogenic soils on terraces in the Primošten vineyards

Results of the mechanical composition indicate that anthropogenic soils of terraces are clayey and fine-grained-clayey, skeletal, medium gravelly to cobbly, while the test area soils are very skeletal. Their water capacity is low, while the air and water permeability capacities are high. The structure of soils in these vineyards is mainly stable and well-defined.

Research results indicate that soils in the Primošten vineyard area contain an average of 156.54 mg of total Cu/kg, 90.54 mg of total Zn/kg and 19.08 g of total Fe/kg. Considering the average concentrations of the metals under research, all soils under research are highly contaminated with zinc (So=0.50), and polluted with copper (So=4.76), according to Bašić (1994).

Concentrations of total copper in the vineyard soils under research range from 138.79 mg/kg to 625.79 mg/kg. Concentrations of this metal in test areas vary from 45.94 mg/kg to 140.01 mg/kg. The highest concentration of total copper was determined in vineyard soil (625.79 mg/kg), and the lowest in test area (45.94 mg/kg) (Figure 1).

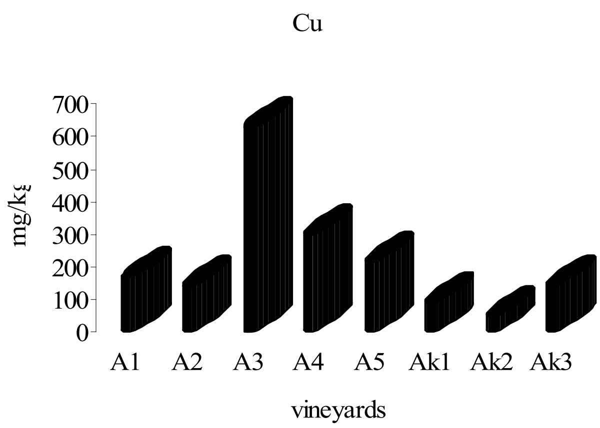

Figure 1 Copper in anthropogenic and forest soils of terraces on cretaceous limestones

Concentrations of total zinc in said vineyard area range from 73.45 mg/kg to 196.50 mg/kg in vineyard soils, while test areas contain from 69.56 mg/kg to 178.63 mg/kg of this metal. The highest concentration of this metal was also determined in vineyard soil (196.50 mg/kg), and the lowest in test area (Figure 2).

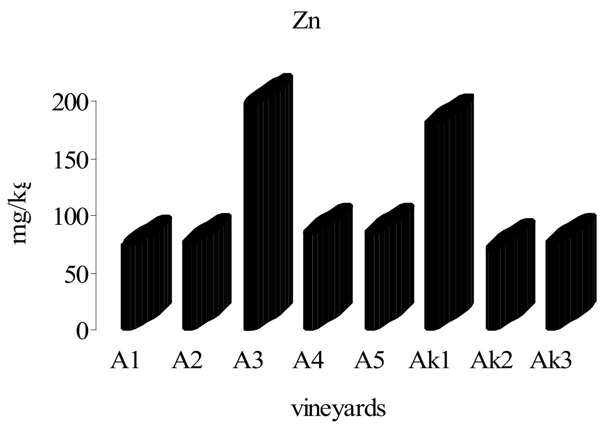

Figure 2 Zinc in anthropogenic and forest soils of terraces on cretaceous limestones

Concentrations of total iron range from 25.08 g/kg to 34.88 g/kg. The highest concentration of this metal was also determined in vineyard soil (34.88 g/kg), and the lowest in test area (Figure 3).

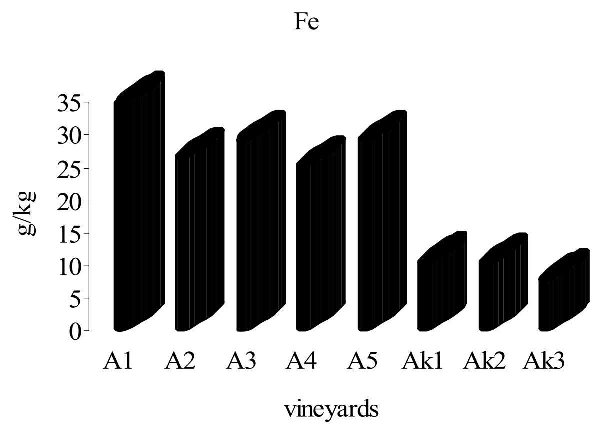

Figure 3 Iron in anthropogenic and forest soils of terraces on cretaceous limestones

Based on the results, we can conclude that all vineyard soils under research in this vineyard area contain a higher total concentration of metals under research in relation to test areas. Based on the variant analysis results ($F_{exp} = 5.60$*), it follows that there is a significant difference in concentrations of total copper between the vineyard and test areas. The determined concentrations of this metal are very significantly higher in vineyard (anthropogenic) soils. Statistically, no significant variances in concentrations of total zinc and iron were identified in the above soils. According to the obtained results, it can be concluded that, due to long-term use of copper fungicides in vineyard soils of Primošten, total copper has accumulated in the surface layer, which corresponds to research results reached by other authors (Gračanin, 1947; Drouineau and Mazoyer, 1962; Delas, 1963; Geoffrion, 1975; Li, 1994; Deluisa et al., 1996; Flores Velez, 1996; Romić Marija and Romić D., 1998; Narimanidze and Bruckner, 1999; Romić Marija et al., 2001; Brun et al., 2003). All vineyard soils under research are contaminated with copper, according to the "By-laws on Protection of Cultivated Land from Contamination by Hazardous Substances" (National Gazette No. 15/1992).

According to the survey results, only two types of copper fungicides are used in Primošten vineyards, four treatments are carried out annually, while the average consumption of water in one vegetative year is 3250 l/ha. Based on this information, concentrations of preparations used and quantities of their active ingredients, it has been calculated that each vegetative year some 4.20 kg of Cu/ha is introduced into these vineyards (Table 2).

preparation	active ingredient	vine succession phases	concentration of individual preparations (%)	quantity of active ingredient (g Cu/l)	total quantity in veg. year (kg Cu/ha)
Bordeaux mixture	copper-hydroxide-potassium sulphate complex	A-B	1.00	200	1.40
Nordox	copper (I) oxide	E,J,L	0.15	750	2.80
					4.20

Table 2 Copper fungicides in use in the Primošten vineyards

Figure 4 shows the mutual relation of total copper and zinc in vineyard soils of the wine-growing area under research, which has been calculated by means of the correlation coefficient (r).

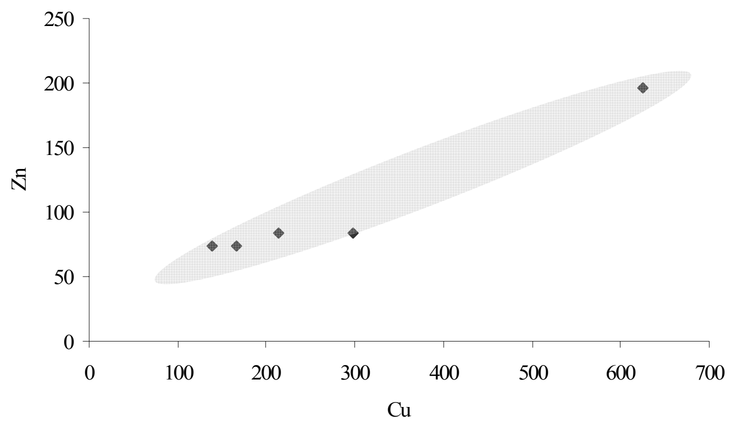

Figure 4 Correlation between total copper and zinc in Primošten vineyard soils

The obtained r_{CuZn} amounts to 0.97. According to the Roemer-Orphal scale (Vasilj, 2000), depending on the value of r-a, the obtained numerical value belongs to the category of fully positive correlation (0.90 – 1.00). By means of the determination coefficient ($d_{xy} = r_{xy}^2$), a part of the variation of total copper in soil has been calculated, which occurs due to variation of total zinc. The determination coefficient in percentages indicates that 94.09% of the total copper variation occurred due to a modified concentration of total zinc in the soil, while the remaining 5.91% was caused by some other factors. Figure 5 shows the mutual relation of total copper and iron, which has also been calculated by means of the correlation coefficient (r).

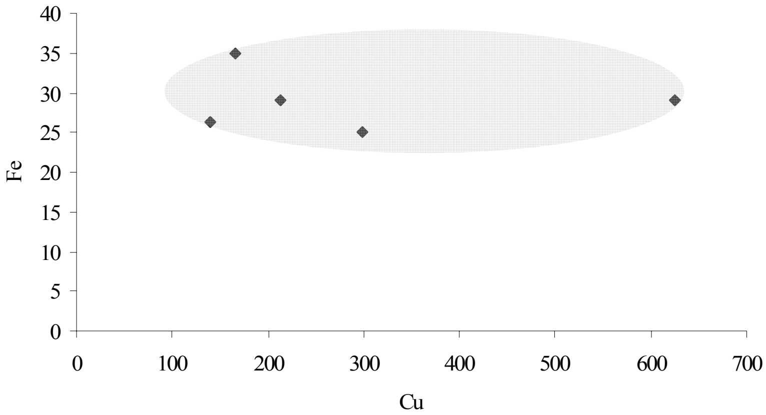

Figure 5 Correlation between total copper and iron in Primošten vineyard soils

The obtained correlation coefficient for total copper and iron amounts to -0.13. This numerical value of the r-a belongs to the category of very weak negative correlation. The determination coefficient d_{xy} has also been calculated in this case. In percentages, it indicates that 1.7% of the total variation of total copper occurred due to a modified concentration of total iron in soil. The balance was caused by some other factors. Results of the research made by Chaignon et al. (2001) partially differ from the results obtained under this research. The authors point out the antagonistic relation between total copper and other metals under research (zinc and iron). Romić Marija (2002) points out that total copper has a high positive correlation with soil organic matter, while total zinc shows no correlation either with any soil properties or with the metals under research. In their research, Narimanidze and Bruckner (1999) reveal a significant correlation among total copper, zinc and led. Parat et al. (2002) conclude that iron is the major factor responsible for accumulation of total copper in clay fraction of soil.

Conclusion

Based on researches made in the Primošten vineyard soils, we can conclude that total copper has been accumulated in the surface soil layer due to long-term use of copper-based fungicides. Concentrations of total copper are significantly higher in all vineyard soils than in test areas. Statistically, no significant variances in concentrations of total zinc and iron were identified in the above soils. An average of 4.20 kg/ha of copper is introduced into these vineyards each vegetative year through vine treatment with copper fungicides. All vineyard soils under research are contaminated with copper, according to the "By-laws on Protection of Cultivated Land from Contamination by Hazardous Substances", while, according to Bašić (1994), they are highly contaminated with zinc and polluted with copper. Total copper and zinc are fully correlated in all vineyard soils under research, while total copper and iron are very weakly negatively correlated.

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