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CONTAMINATION OF KASTELA BAY VINEYARD SOILS WITH HEAVY METALS

ONEČIŠĆENOST VINOGRADARSKIH TALA KAŠTELANSKOG ZALJEVA TEŠKIM METALIMA

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ABSTRACT

Long-term use of copper fungicides in wine-growing causes increased accumulation of total copper in the surface layer of soil. Many an author has researched the anthropogenic influx of copper and other heavy metals in vineyard soils, which can result in environmental risks. The objective of the research was to identify concentrations of total copper, zinc and iron in various types of vineyard soils of the Kaštela Bay wine-growing area, and to estimate their suitability for environmental production in order to conserve the eco-system, because no researches of this type have been made in Dalmatia to date.

Key words**:** heavy metals, vineyard soils, contaminated soils, environmental production

SAŽETAK

Dugogodišnja uporaba bakrenih fungicida, u vinogradarstvu, dovodi do povećanog nakupljanja ukupnog bakra u površinskom sloju tla. Mnogi autori istraživali su antropogeni unos bakra i drugih teških metala, u vinogradarska tla, koji mogu rezultirati rizikom za okoliš. Cilj istraživanja bio je utvrditi koncentracije ukupnog bakra, cinka i željeza u različitim tipovima vinogradarskih tala Kaštelanskog zaljeva te procijeniti njihovu pogodnost za ekološku proizvodnju u svrhu očuvanja ekosustava, jer do sada, u Dalmaciji nisu provedena istraživanja ovog tipa.

Ključne riječi**:** teški metali, vinogradarska tla, onečišćena tla, ekološka proizvodnja

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INTRODUCTION

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 with 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. Copper fungicides have been in use in wine-growing as plant-protection products against fungal diseases since the 18th century (Lafforgue, 1928). In Croatia, there are numerous copper-based preparations permitted for use in wine-growing for protection against fungal diseases (Glasilo biljne zaštite [Plant Protection Courier], 2006). According to information gathered to date, long-term use of copper fungicides in wine-growing results in ingression of significant quantities of copper, which remains in the surface soil layer at 0-15 cm, as confirmed by a number of researches (Gračanin, 1947; Drouineau and Mazoyer, 1962; Delas, 1963; Geoffrion, 1975; Li, 1994; Deluisa et al., 1996; Flores Velez et al., 1996; Romić Marija and Romić D., 1998; Narimanidze and Bruckner, 1999; Romić Marija et al., 2001; Romić Marija, 2002; Brun et al., 2003). It should be pointed out that long-term fertilization and use of some other plant-protection products also results in accumulation of significant quantities of other heavy metals in soil (Romić M. and Romić D., 2003; Mirlean et al., 2006). The factors which affect the distribution and migration of heavy metals in agricultural soil profiles are: type of soil, in spite of its morphogenetic properties being impaired by treatment; changes in sequence of genetic horizons and active profile depth; quantity of organic matter and pH reaction; wear processes and accumulation of clay and Fe and Mn oxides; and either geogenic, pedogenic or anthropogenic origin of elements (Vukadinović and Lončarić, 1998).

MATERIAL AND METHODS

Sampling in the Kaštela Bay area was made on three different locations, depending on the type of anthropogenic soil (colluvial, flysch, and terra rossa). Areas with anthropogenic colluvial soils were selected for location A (N43^{o}53', E16^{o}43'). Location B comprised areas with anthropogenic soils on flysch (N43^{o}56', E16^{o}33'), while areas with anthropogenic soils on terra rossa were selected for location C (N43^{o}55', E16^{o}28'). Five representative vineyards were selected from each of the A, B and C locations, as old and as large as possible, in view of the issue of fragmentation of agricultural soils in the area. Three test areas (Ak, Bk and Ck) were also selected in each location – forest soils which had never been exposed to application of copper-based plant-protection products, in order to determine the so-called background concentration.

Soil was sampled in each vineyard and on each test area. Average samples were taken by a 30-mm dia cylindrical probe from the surface layer (0-20 cm) (Škorić, 1965; Brun et al., 2001). Total copper, zinc and iron contents were determined by atomic absorption spectrophotometry with flame (Varian 220). All indicators were processed by the statistical method of variant analysis (ANOVA), by means of the STATVIEW software (SAS program package, version 5.0).

RESULTS AND DISCUSSION

Copper, Zinc and Iron in Soils Under Research

Table 1 shows that total copper concentrations in vineyard soils in this location range between 70.50 mg/kg and 181.62 mg/kg, while concentrations from 21.85 mg/kg to 49.05 mg/kg were recorded in test area soils. Concentrations of total zinc in vineyard soils range from 47.71 mg/kg to 171.37 mg/kg, and in the soils of the test areas from 33.21 mg/kg to 111.41 mg/kg. Concentrations of total iron vary from 9.27 g/kg to 16.26 g/kg in vineyard soils, whereas in test area soils they range from 7.76 g/kg to 12.83 g/kg. The highest average concentrations of the metals under research were identified in vineyard soils of location A.

Table 1. Cu, Zn and Fe in the surface layer of anthropogenic colluvial soils

Vineyard/test area	Cu (mg/kg)	Zn (mg/kg)	Fe (mg/kg)
A1	70.50	171.37	9.27
A2	71.84	105.42	16.26
A3	106.19	74.92	15.55
A4	85.40	83.97	12.21
A5	181.62	47.71	10.14
Ak1	45.53	94.94	12.83
Ak2	21.85	33.21	7.76
Ak3	49.05	111.41	9.84

According to the results shown in Table 2, anthropogenic soils on flysch contain from 163.68 mg Cu/kg to 302.05 mg Cu/kg, while the concentrations of this metal in forest soils range from 44.42 mg/kg to 124.77 mg/kg. Concentrations of total zinc range from 34.22 mg/kg to 130.14 mg/kg in vineyard soils, while forest soils contain from 68.91 mg/kg to 89.58 mg/kg of this metal. Concentrations of total iron range from 11.35 g/kg to 41.40 g/kg in vineyard soils, and from 9.43 g/kg to 14.94 g/kg in test area soils. The highest average concentrations of said metals were also identified in vineyard soils in location B.

Table 2. Cu, Zn and Fe in the surface layer of anthropogenic soils on flysch

Vineyard/test area	Cu (mg/kg)	Zn (mg/kg)	Fe (mg/kg)
B1	204.86	106.37	17.05
B2	211.46	86.26	19.02
B3	183.33	72.20	13.71
B4	302.05	130.14	41.40
B5	163.68	34.22	11.35
Bk1	57.42	89.58	9.43
Bk2	124.77	75.05	14.94
Bk3	44.42	68.91	10.04

Table 3 shows that concentrations of total copper range from 113.46 mg/kg to 252.89 mg/kg in vineyard soils, and from 52.03 mg/kg do 290.11 mg/kg in test area soils. Concentrations of total zinc in vineyard soils range from 63.62 mg/kg to 115.04 mg/kg, while forest soils contain from 65.82 mg Zn/kg to 92.70 mg Zn/kg. Concentrations of total iron range from 18.95 g/kg to 29.12 g/kg in vineyard soils, and from 22.61 g/kg to 31.13 g/kg in test area soils. The highest average concentrations of the metals under research were also identified in vineyard soils of this location (C).

It can be concluded from all results that total concentrations of all metals under research are higher in vineyard soils than in those in test areas. Concentrations of total copper in vineyards are pretty higher than those in forest soils, as opposed to concentrations of total zinc and iron, where such differences are negligible. Concentrations of total copper in anthropogenic soils on flysch are somewhat higher than in other anthropogenic soils under research (colluvial

Table 3. Cu, Zn and Fe in the surface layer of anthropogenic soils on terra rossa

Vineyard/test area	Cu (mg/kg)	Zn (mg/kg)	Fe (mg/kg)
C1	252.89	99.49	27.95
C2	248.37	86.11	29.12
C3	162.23	115.04	22.60
C4	196.47	88.78	27.30
C5	113.46	63.62	18.95
Ck1	52.03	67.14	27.78
Ck2	53.32	65.82	31.13
Ck3	290.11	92.70	22.61

and on terra rossa), while concentrations of total zinc are somewhat higher in colluvial anthropogenic soils and on flysch than in anthropogenic soils on terra rossa. The results of total iron concentrations equal those of Gračanin (1947), revealing that terra rossa soils are rich in total iron and that they can contain up to 20% more of this metal than other soils.

Significance of Variances in Concentrations of Researched Metals between Anthropogenic and Forest Soils

Based on the variant analysis results ($F_{exp} = 12.895^{*} > F_{tab\ 0.05} = 9.28$), it follows that there is a significant difference in concentrations of total copper between the vineyard and forest soils. Significantly higher concentrations of this metal were identified in vineyard (anthropogenic) soils. Statistically, no significant variances in concentrations of zinc and iron were identified in the above soils (Table 4).

Table 4. Results of variant analysis of concentrations of researched metals in vineyard and forest soils

	Cu (mg/kg)	Zn (mg/kg)	Fe (g/kg)
Vineyard (anthropogenic) soils	a*	ns	ns
Forest soils	b	ns	ns

**- significant variance between different letters (for e < 0.05); ns – not significant*

It can be concluded that, due to long-term use of copper fungicides in vineyard soils, total copper accumulates in the surface layer in Dalmatia as well, which cannot be said for concentrations of total zinc and iron. Their accumulation is conditioned by some other factors. The results of these researches match those obtained earlier by a number of authors (Gračanin, 1947; Drouineau and Mazoyer, 1962; Delas, 1963; Anić, 1973; Geoffrion, 1975; Li, 1994; Deluisa et al., 1996; Flores Velez, 1996; Brun et al., 1998; Romić Marija and Romić D., 1998; Narimanidze and Bruckner, 1999; Romić Marija et al., 2001; Brun et al., 2003).

Considering the average concentrations of the metals under research, all soils under research are highly contaminated with zinc (So=0.60), and polluted with copper (So=3.40), according to Bašić (1994). According to the "By-laws on Protection of Cultivated Land from Contamination with Hazardous Substances" (National Gazette No. 15/1992), each vineyard under research is contaminated with copper, and contains total copper in excess of the maximum allowed values as prescribed by the "By-Laws on Environmental Production in Plant Cultivation and Manufacture of Plant Products" (National Gazette No. 91/2001). According to the said By-laws (National Gazette No. 91/2001), only one vineyard soil in location A contains total zinc in excess of the maximum allowed values.

Significance of Variances in Concentrations of Researched Metals in Various Types of Anthropogenic Soils

Statistically, by means of variant analysis, no significant differences in concentrations of total copper and zinc were identified among vineyard soils in locations under research (Table 5). The obtained results ($LSD_{exp} = 2.687^* > LSD_{tab\ 0.05} = 2.120$) indicate a significant difference in total iron concentrations between colluvial anthropogenic soils and anthropogenic soils on terra rossa. The obtained differences are significant with a 5% margin of error. Significantly higher concentrations of this metal were identified in vineyard soils on terra rossa. These are clay loam and silty clay loam soils. These soils are also heavier in relation to colluvial anthropogenic soils, and therefore it is our conclusion that leaching of this metal into lower layers is lesser and slower. The results of total iron concentrations equal those of Gračanin (1947), showing that terra rossa soils are rich in iron.

Table 5. Results of variant analysis of concentrations of researched metal in soils

Location	Soil	Cu (mg/kg)	Zn (mg/kg)	Fe (g/kg)
A	anthropogenic colluvial soils	b	ns	b
B	anthropogenic soils on flysch	ab	ns	ab
C	anthropogenic soils on terra rossa	ab	ns	a*

* - significant variance between different letters (for e < 0.05);
** - very significant variance (for e < 0.01); ns – not significant

CONCLUSION

Based on researches made in the Kaštela Bay vineyard soils, we can conclude that total copper has 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 forest soils. Statistically, no significant variances in concentrations of total zinc and iron were identified in the above soils. All vineyard soils under research are contaminated with copper, according to the "By-laws on Protection of Cultivated Land from Contamination with Hazardous Substances", while, according to Bašić (1994), they are highly contaminated with zinc and polluted with copper. All soils under research contain total copper in excess of the maximum allowed values as prescribed by the "By-Laws on Environmental Production in Plant Cultivation and Manufacture of Plant Products" (National Gazette No. 91/2001). According to said By-Laws (National Gazette No. 91/2001), only one vineyard soil contains total zinc in excess to the maximum allowed values. The results indicate that significantly higher concentrations of iron were identified in vineyard soils on terra rossa, while statistically no significant differences of total copper and zinc were identified among vineyards soils in locations under research. Considering the obtained results, switching over to environmental production is not possible for the time being. The results of this research are a contribution to the inventory of heavy metals in vineyard soils of Central Dalmatia. They will also provide clues to the current contamination status, in order to conserve the eco-system.

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