

Modification of Macronutrients and Copper Content from Soil Before and After Phytosanitary Treatments in Vineyard from Tohani-Dealu Mare

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This research was developed in order to study the copper total and mobile contents before and after copper based treatments in some vineyard plots from Tohani-Dealu Mare. The studies revealed that total form for copper is higher than allowable level imposed by Romanian legislation, but below alert level according to the same legislation. Also, it was found that total copper content is higher in upper layers. Mobile form for copper is over 1.5 mg/kg that express a high content, for all soil samples. This can be a consequence of long term copper fungicides treatments. In order to establish the level of macronutrients in soil, for all samples were determined humus content, mobile phosphorus and potassium using standardised methods.

Keywords: copper, vineyard, fungicides, copper hydroxide, copper oxychloride

Inorganic copper compounds have been widely used for a long time as fungicides against downy mildew (*Plasmopara Viticola*). A large quantity of copper sprayed on the vine reaches the soil, where it often remains fixed in the surface layer. The elevated concentration in the soil surface due to fungicide spraying has been reviewed during time [1, 2]. Even if synthetic organic fungicides are banned in European viticulture, fungicides that contain copper (copper hydroxide, copper oxychloride, copper sulphate) are allowed and very useful for organic vine cultivation but in limited doses [3]. In soil, copper is accumulated mainly in the upper layer because of its tendency to bind carbonates, organic matter, hydrated oxides of Fe, Al, and Mn [4]. As copper it seems to accumulate near the surface of the soil, the grapevines with a deep root system are not affected. Copper mobility along the soil profile and bioavailability for root uptake depend on soil pH, cation exchange capacity, organic matter, texture [5-7].

The availability of copper is relatively low at pH 6.5-7 [8] since the mobility of the majority of heavy metals decreases as pH increases due to the precipitation of insoluble forms as hydroxides, carbonates and organic complexes.

The values of total content of copper in vineyard soils, according to literature studies, range between 30-250 mg/kg in Southern France [9], 400-500 mg/kg in vineyards of Alsace, Champagne and Burgundy [10,11], up to 800 mg/kg in areas of Bordeaux [12], 10-250 mg/kg in vineyards from Australia [13], 9.1-100 mg/kg in vineyards from Taiwan [14], 2-375 mg/kg in Italy [15].

Estimation of copper total content in soils and, particularly in vineyard soils, is an important step for quantification of the pollution level but assessment of the mobile form is equally important to determine the availability of copper accumulated in vineyards [16].

Evaluation of mobile copper is worldwide assessed using various extractive solutions or mixtures: DTPA [9, 17-21], CaCl₂ [9], EDTA [9, 21-23]. In Romania, mobile form of copper is usually assessed through a method developed in [24].

According to Romanian legislation [25], maximum allowable level for total copper content from soil is 20mg/kg, alert threshold is set at 100mg/kg for sensitive areas (residential and agricultural) and 250mg/kg for less sensitive areas (commercial and industrial). Intervention threshold for copper is 200mg/kg for sensitive area and 500mg/kg for those less sensitive.

The objectives of this research are evaluation of copper content before and after vineyard treatments for some plots selected from vineyard Tohani-Dealu Mare. Also, for soil samples are usually determined the concentrations of major macronutrients and as consequence, we carried out the humus content, mobile phosphorus and potassium levels for all soil samples through methods often used in our country.

Experimental part

Soil sampling

The investigation was carried out during 2009 on vineyard plots from vineyard Tohani-Dealu Mare, a vineyard of almost 20 years old. There were analysed soils from six plots where are different varieties of vines: Tămâioasă Românească, Sauvignon Blanc, Busuioacă de Bohotin, Italian Riesling, Fetească Albă, Fetească Neagră. The soil analyses were performed for samples collected from 0-20 cm and 20-40 cm depth. Prior to analysis, the soil samples were air dried, lightly grounded and sieved through 2 mm nylon sieve.

Chemical analyses

The soil samples have been analyzed from the point of view of general agrochemical parameters as pH, mobile forms of phosphorus and potassium, humus and also total and mobile forms for copper. The soil reaction was carried out through potentiometric method in aqueous suspension, 1:2.5 (w/v).

Humus content was determined by the oxidimetric method developed by Walkley-Black-Gogoșă. Mobile phosphorus content was evaluated by spectrophotometric

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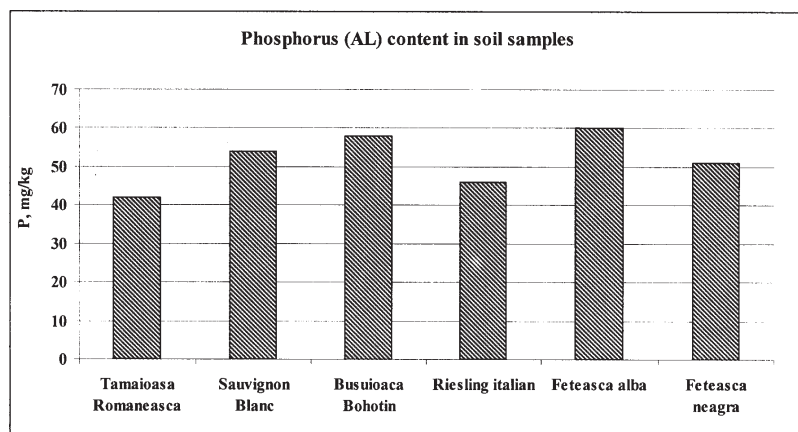


Fig. 1. Phosphorus (AL) content in soil samples

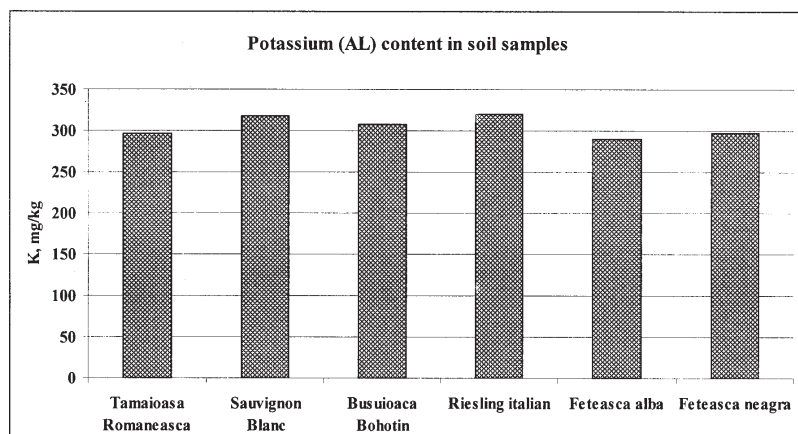


Fig. 2. Potassium (AL) content in soil samples

molybdenum blue method using as extracting solution ammonium acetate-lactate (AL) at pH 3.7 (Egner-Riehm-Domingo method). The mobile form of potassium was quantified in the same extract (AL) by flame photometry.

The total content for copper was assessed by FAAS technique (Zeenit 700, Analytic Jena). The soil sample was processed according to a method already published [17] and was microwave digested using a microwave Milestone Ethos Pro apparatus. The mobile form of copper was quantified by FAAS means according to method developed in [24].

All analyses were performed in duplicate and the reported value is the average. The calibration curve for copper is linear for the studied ranges and was plotted by running different concentrations of standard solutions. For calibration curve was used stock solution of 1000 ppm copper provided by Merck.

All the materials and vessels that were used were kept at least 24 h in a plastic container filled with HNO₃ 10% v/v and washed for several times with deionised water.

All reagents used during this research were of analytical grade. Stock standard solutions were freshly prepared from standard solutions provided by Merck.

The used ultra pure water for samples analytic preparation was obtained with a Simplicity system from Millipore.

Vineyard treatments

The first group of analyses, T₀, was done using soil samples that were taken at 20.06.2010, one month after treatments with some copper free products as Mancozeb, Fenazaquin, Dinocap, Metiram, Pyraclostrobin, Cypermethrin in different application schemes.

Treatment T₁ was applied on 30.06.2010 and contained commercial products that had as active substances Mancozeb, sulphur, tebuconazol, propargit, iprovalicarb,

copper oxychloride. Soil samples were taken on 19.07.2010 and were analysed after sampling.

Treatment T₂ was applied on 20.07.2010 and was composed of copper hydroxide, sulphur, cyprodinil, dicloran, pyraclostrobin, tebuconazole. Soil samples were taken on 10.08.2010.

All soil samples were analysed immediately after their sampling.

It is known that in vineyards from Romania are applied 6-7 treatments (two without copper), 3-4 against other diseases and 2 against gray mould (*Botrytis bunch rot*). Also there are involved in treatment scheme other 1-3 interventions for protection against spiders and 3 spraying procedures with insecticides [26].

Results and discussions

Mobile phosphorus (P_{AL}) ranges between 42-60 mg/kg for all soil samples (fig. 1), meaning a weak content for vineyards, in the meantime potassium concentration (K_{AL}) ranges between 290-320 mg/kg for all soil samples (fig. 2), a good content for vineyards. Humus content, found very low, is in the range 1.62-2.10% for all soil samples (fig. 3).

The copper contents (total form) obtained after chemical analyses are presented in figure 4. The found level for total copper at 0-20 cm depth is higher (mean value, 73.94 mg/kg) than at 20-40 cm depth (mean value, 62.48 mg/kg), this being in agreement with some results presented in literature [20].

All copper contents (total form) are higher than 20 mg/kg, maximum allowable limit set by Romanian legislation [25] but below alert threshold according to the same legislation. Anyway, this copper content is normal for a vineyard soil, taking into account that in this area are applied copper compounds as fungicides for a long time. The repeated use of Cu compounds as fungicides to control

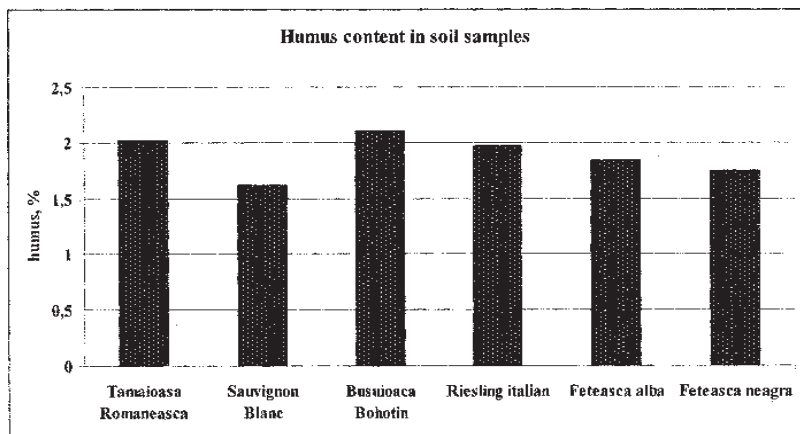


Fig. 3. Humus content in soil samples

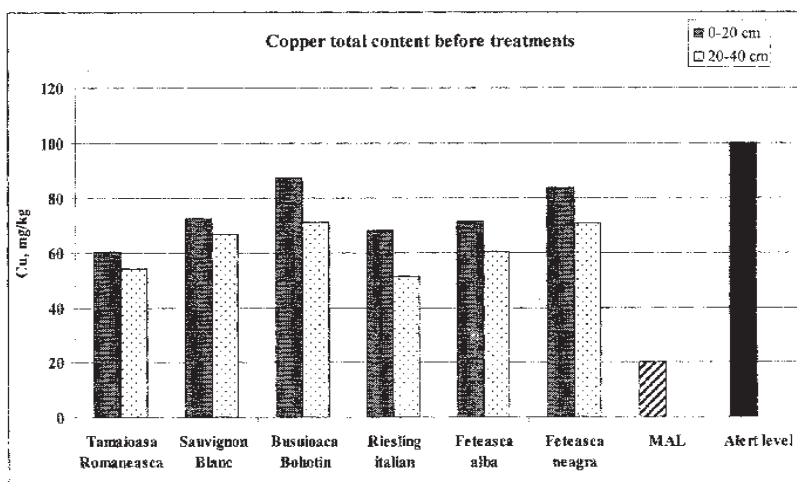


Fig. 4. Copper total content before treatments

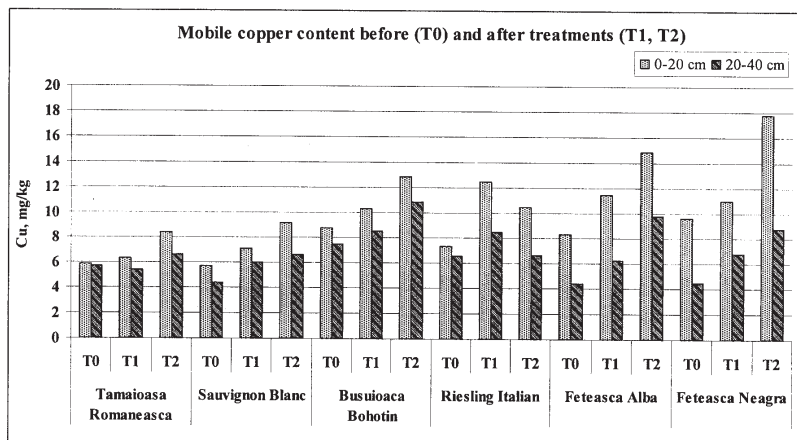


Fig. 5. Mobile copper content before (T0) and after treatments (T1, T2)

vine downy mildew has been responsible for the heavy increase of total Cu content in vineyard soils.

In the literature there are studies where are presented copper contents that are higher [13, 14] and much higher [10-12] than those found by us, where almost that became an environmental issue.

The same variation was observed for mobile form, as well (fig. 5). The concentrations for mobile copper before treatments are high, over 1.5 mg/kg, which express a high content [24]. This behaviour could be correlated with slightly acidic soil reaction.

Before treatments, in all soil samples the copper contents (mobile form) are higher at 0-20 cm than in 20-40 cm layer. At 0-20 cm depth, copper ranges between 5.71 and 9.58 mg/kg and at 20-40 cm, the same parameter is between 4.36 and 7.43 mg/kg.

After the first treatment, it can be observed that mobile copper content increased in an evident manner for all samples for 0-20 cm depth. Additionally, for 20-40 cm

depth were observed elevated values than initial ones, with the exception of soil sample (1) where it was recorded a slight decrease.

The soil reaction before treatments is slightly acidic to neutral. After the first treatment, it was noticed an increase of pH value, perhaps due to the compounds used to treat vineyard (fig. 6).

After the treatment T₂, mobile copper concentrations increased in 0-20 cm layer for all samples with the exception of soil sample (4). A significant increase was recorded for sample (6).

Copper distribution with soil depth showed that Cu input from Cu treatment was essentially concentrated in the upper layers. This behaviour is consistent with other studies presented in literature [20].

Interesting studies regarding copper content in vine leaves, grapes and wine selected from the same vineyard plots and correlated to copper content from soil are in development and will be published soon.

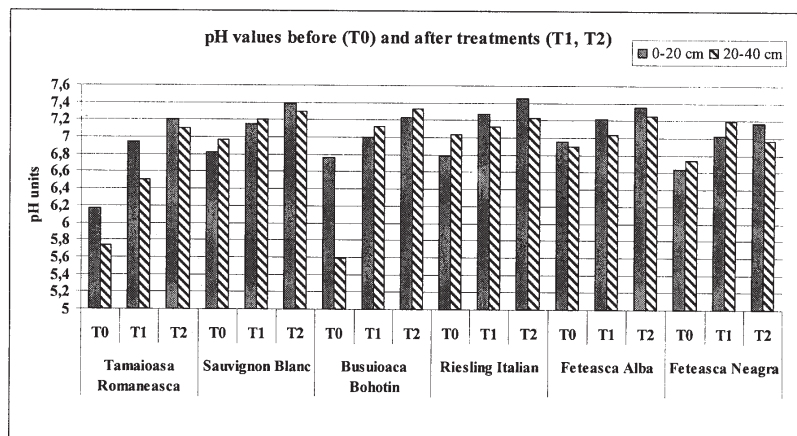


Fig. 6. Soil reaction before and after treatments

Conclusions

Developed studies regarding copper content in vineyard from Tohani-Dealul Mare, revealed that total copper levels in all six plots exceeded maximum allowable level for 0-20 cm and 20-40 cm depth, but are below alert level. These results were expected taking into account that copper compounds were applied during time for vineyard treatments.

The found copper concentrations revealed that copper is accumulated more in surface layer (0-20 cm), behaviour that was predictable and is in agreement with literature review.

With an exception, the same variation was found for mobile copper. This form is also higher than value that expresses high mobile copper content.

Moreover, for all soil samples were assessed mobile phosphorus and potassium levels that were found to be weak content and good content, respectively. Humus level for all soil samples ranges between 1.62-2.10%.

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Manuscript received: 23.02.2011