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Copper and lead residues in olives after olive tree treatments with three different copper formulations

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INTRODUCTION

Field tests were performed to control two olive fungal diseases known as olive anthracnose *Collectotrichum spp*, and olive leaf spot, *Spilocaea oleagina* (Cast.), and to evaluate the pesticide residues in the olive fruits harvested at different times. The experiment was carried out in a Cv Cobrançosa olive orchard located near Mirandela, Nordeast of Portugal. The orchard was subdivided in four plots, three of them for application of different copper preparations (Bordeaux mixture Valles – copper sulphate and $Ca(OH)_2$, Kocide DF- copper hydroxide, and Curenox 50 – copper oxychloride) and one as control. In the middle of October the different plots were sprayed with the aqueous suspensions of the pesticides prepared following the supplier indications, i.e., $CuSO_4$ +$Ca(OH)_2$ (20% Cu), $Cu(OH)_2$ (40% Cu), $Cu(OCl)_2$ (50% Cu), and water, respectively. After treatment, at different times - four hours, 8, 13, 28 and 44 days - five trees were randomly selected in the middle of each plot, and 60 olive fruits per tree were collected in plastic bags and stored at –20ºC until copper analysis. The olives were washed with tap water, the stones removed with decontaminated plastic material, the samples dried in a stove, pulverized and heat digested with H_2O_2 plus HNO_3 mixture. Other heavy metals, namely lead, nickel and cadmium, were also considered to evaluate the putative residues present in the olive fruits due to the impurities of the pesticide formulations. The metal contents were measured by atomic absorption spectrometry with graphite furnace.The aim of this work was to evaluate the pesticide residues in olives harvested at different times after the application of three different copper products.

METHODS

The experiment was carried out in a *Cv.* Cobrançosa olive orchard located near Mirandela, Northeast of Portugal.

The orchard was subdivided in four plots, three of them for application of three different copper preparations (Bordeaux mixture Valles – copper sulphate and calcium hydroxide, Kocide DF- copper hydroxide, and Curenox 50 – copper oxychloride) and one as control. In the middle of October the different plots were sprayed with the aqueous suspensions of the pesticides prepared following the supplier indications, i.e., $CuSO_4$ +$Ca(OH)_2$ (20% Cu), $Cu(OH)_2$ (40% Cu), $Cu(OCl)_2$ (50% Cu), respectively. A control group of olive trees was only sprayed with water. After treatment, at different times - four hours, 8, 13, 28 and 44 days - five trees were randomly selected in the middle of each plot, and 60 olive fruits per tree were collected and stored in plastic bags at –20ºC until copper analysis. The olives were washed with tap water, the stones removed with decontaminated plastic material, the samples dried in a stove, pulverized and heat digested with H_2O_2 plus HNO_3 mixture. The copper and lead contents were measured by atomic absorption spectrometry with graphite furnace (1).

Table 1.Contents (mean values) of Cu and lead

Cu µg/g dry olive fruits				
Time (days)	$CuSO_4$ + $Cu(OH)_2$ (20% Cu)	$Cu(OH)_2$ (40% Cu)	$Cu(OCl)_2$ (50% Cu)	H_2O
0	34,4	30,1	63,9	8,5
8	28,4	21,7	33,9	9,6
13	23,3	20,6	26,2	8,5
28	20,3	11,5	20,1	7,7
44	14,5	16,9	23,9	7,9
Pb µg/kg dry olive fruits				
0	21,0	26,5	36,0	21,7
44	<11,0	<11,0	<11,0	<11,0

RESULTS

In spite of the different copper concentrations of the applied pesticides, olive copper residues were similar for the CuSO4 +$Ca(OH)_2$ (20% Cu) and $Cu(OH)_2$ (40% Cu) applications (from 34.4 µg/g to 14.5 µg/g and from 30.1 to 16.9 µg/g, respectively). Copper contents were about the double in the olive fruits treated with $Cu(OCl)_2$ (50% Cu) product (from 63.9 to 23.9 µg/g). For the first three collection times, the copper contents of the olives from the $Cu(OCl)_2$ treated trees were significantly higher than those collected from the control trees sprayed with water (from 7.7 to 9.6 µg/g). At the 4 h harvesting time, the olives treated with $Cu(OCl)_2$ presented copper contents significantly higher than olives treated with the two other formulations.

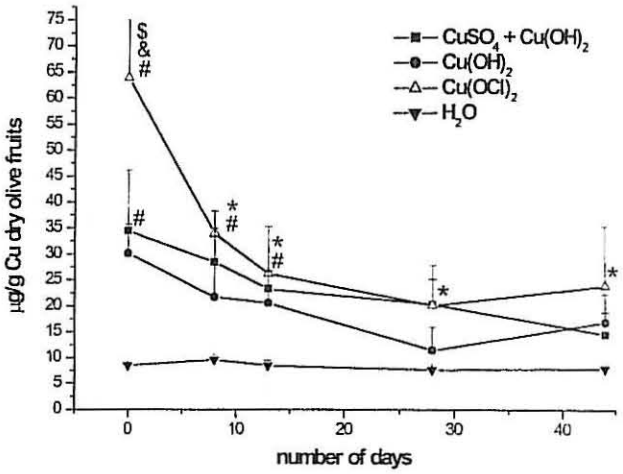

Figure 1. Olive Cu contents (µg/g dry olive fruits) after 0, 8, 13, 28 and 44 days of each treatment. Results are given as mean ± SD. Cu contents were compared by two way analysis of variance (ANOVA; between groups) followed by the Scheffé Test. The level of significance was set at $P < 0.05$. #compared with H_2O; &compared with $CuSO_4$ + $Cu(OH)_2$; $compared with $Cu(OH)_2$; *compared with time zero days within each treatment.

CONCLUSIONS

1. The treatment of olive trees with copper pesticides can significantly increase the metal levels of the olive fruits and the resulting olive oils.

2. The copper pesticide formulations should not be applied to the olive trees near the harvesting period in order to avoid additional copper contamination.

3. It is not indifferent to treat the olive trees diseases with any of the applied copper formulations as it is demonstrated by the metal residues levels of the samples treated with the most concentrated copper formulation. In this case, after 13 days of the application, the olives had still copper contents significantly higher than the control one.

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Field tests were performed to control two olive fungal diseases known as olive anthracnose, *Colletotrichum spp.*, and olive leaf spot, *Spilocae oleagina* (Cast.) and to evaluate the pesticide residues in the olive fruits harvested at different times. The experiment was carried out in a *Cv.* Cobrançosa olive orchard located near Mirandela, Northeast of Portugal. The orchard was subdivided in four plots, three of them for application of three different copper preparations (Bordeaux mixture Valles – copper sulphate and calcium hydroxide, Kocide DF- copper hydroxide, and Curenox 50 – copper oxychloride) and one as control. In the middle of October the different plots were sprayed with the aqueous suspensions of the pesticides prepared following the supplier indications, i.e., $CuSO_4$ +$Ca(OH)_2$ (20% Cu), $Cu(OH)_2$ (40% Cu), $Cu(OCl)_2$ (50% Cu), and water, respectively. After treatment, at different times - four hours, 8, 13, 28 and 44 days - five trees were randomly selected in the middle of each plot, and 60 olive fruits per tree were collected in plastic bags and stored at –20°C until copper analysis. The olives were washed with tap water, the stones removed with decontaminated plastic material, the samples dried in a stove, pulverized and heat digested with H_2O_2 plus HNO_3 mixture.
Other heavy metals were also considered to evaluate the putative residues present in the olive fruits due to the impurities of these pesticide formulations. Lead, nickel and cadmium were selected for monitoring after four hours and 44 days of the treatment. The metal contents were measured by atomic absorption spectrometry with graphite furnace.
Although the different copper concentrations of the applied pesticides, olive copper residues were similar for the $CuSO_4$ +$Ca(OH)_2$ (20% Cu) and $Cu(OH)_2$ (40% Cu) applications (from 34.4 µg/g to 14.5 µg/g and from 30.1 to 16.9 µg/g, respectively, for the five time collections). Copper contents were about the double in the olive fruits treated with $Cu(OCl)_2$ (50% Cu) product (from 63.9 to 23.9 µg/g). Olives from all the treated trees had at all the collection times copper contents significantly higher than those of tree controls sprayed with water, ranging the values from 7.7 to 9.6 µg/g. Referring to the other metals, lead levels were significantly higher in the first harvesting than after 44 days. For cadmium and nickel there was no differences in their contents.
In conclusion, the treatment of olive trees with copper pesticides can significantly increase the copper levels of the olive fruits and the resulting olive oils as well as the contamination with lead.