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Original scientific paper

Effects of copper citrate as a defoliant in nursery fruit stock production

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SUMMARY

The effects of copper citrate on defoliation of one year old fruit stocks in a nursery are presented in this paper. The investigation aimed to evaluate the defoliation efficacy of copper citrate as a new formulation, compared with other compounds recommended for that purpose. Field trials were conducted in the region of Trstenik, a center of nursery production in Serbia in 2016 and 2017. Two years of investigation showed that copper citrate could be used as an efficient compound for defoliation in nursery production. A stronger defoliation effect was observed on plum stocks, compared to apple stocks. Better results were achieved with the highest concentration of copper citrate (2%), while the effectiveness decreased with lower concentrations (0.5%, 1.0% and 1.5%). Defoliation degree on nursery apple stocks after treatment with 2.0% concentration of copper citrate varied from 80.6% to 95.6%, while it reached 100% on plum stocks.

Keywords: Copper; Defoliation; Nursery production; Fruit stocks

INTRODUCTION

Copper (Cu) is an essential redox-active transition metal which is involved in many physiological processes in plants because it can exist in multiple oxidation states *in vivo*. Under physiological conditions Cu exists as Cu^{2+} or Cu^{+} (Yruela, 2005). Cu^{2+} and Cu^{+} ions are soluble in water and provide antifungal and antibacterial effects (biostatic elements) at low concentrations, and their contribution to the production of pesticides has so far been irreplaceable. A peak in production and use of pesticides based on copper was in the middle of the 20th century. Over the past several decades pesticide-producing corporations have been manufacturing pesticides with copper in the forms of sulphates, oxychlorides, hydroxides, oxides, etc. The efficiency of copper pesticides, which are particularly aggressive in moist media, is caused by denaturation of protein structures (secondary and tertiary) of fungi and bacteria, and consequent interruption of their functions (Rusjan, 2012).

Copper compounds are widely used for plant protection, primarily as fungicides and bactericides for fruit, vegetable, ornamental and field crops (Andersen et al, 1991; Scheck & Pscheidt, 1998; Agrios, 2005; Fishel, 2005; Ivanović &

Ivanović, 2005; Aleksić et al., 2012; Rusjan, 2012; Popović et al., 2014). In all its different chemical forms copper remains one of the most important agents for pathogen control in horticulture (due to its broad activity spectrum, unspecific mode of action, low risk of resistance and compatibility with organic production); and its use should therefore be controlled and adapted to environmentally-sound conditions and plant necessities (Rusjan, 2012).

Copper citrate is a complex compound of copper, which is characterized by a high degree of dissociation in relation to other copper compounds that have been applied so far, and it can be used at lower concentrations (Popović et al. 2013; 2014). Copper citrate has already shown a significant ability to inhibit mycelial growth and germination of *Venturia inaequalis* ascospora (Aleksić et al. 2013), and to inhibit mycelial growth of *Monilia laxa* (Popović et al. 2013). This compound has no toxic effects on fish, birds, mammals or bees and can be used as an environmentally acceptable agent for plant protection (Georgopoulos et al. 2001). At high concentrations, Cu may become toxic, causing symptoms such as chlorosis and necrosis, stunting, leaf discoloration and inhibition of root growth (van Assche & Clijsters, 1990; Marschner, 1995).

Fruit growing is an agricultural branch with a very long tradition and great economic importance in Serbia. In recent years, we have witnessed an expansion of fruit stock cultivation area (FAOSTAT, 2017), which has caused a related increase in the production of planting material. The process of defoliation, which precedes extraction, classification and heeling-in of nursery stocks, is one of the most important tasks in nursery production. Defoliation can be conducted in several ways. Natural defoliation is the best and most practical way that implies temperatures below zero and hoarfrost during the optimal period prior to the extraction of nursery fruit stocks. However, hoarfrost and temperatures below zero have occurred late in recent years, so that producers had to apply other methods of defoliation. One of such methods is mechanical defoliation, which is labor-intensive and increases production cost. The use of some chemical compounds is yet another method of defoliation. The application of copper formulations for control of phytopatogenic fungi under field conditions causes problems with phytotoxic effects (Jamar & Lateur, 2007; Kurnik et al. 2011; Aleksić et al. 2012). As a result, copper-based preparations are most frequently used as defoliation compounds, especially those based on copper sulfate, which causes rapid defoliation. The objective of this study was to evaluate the potential of another copper compound, copper citrate, as a possible solution for defoliation in nursery production of fruit stocks.

MATERIAL AND METHODS

The efficiency of copper citrate as a defoliant was examined in nurseries in Ljubava and Milutovac, Serbia, during 2016 and 2017. Nursery stocks of apple (cv. *Gala*) were treated in Ljubava, and stocks of apple (cv. *Gala*) and plum (cv. *Stanley*) were treated in Milutovac. Copper citrate was synthesized in the chemical laboratory of the Institute for Plant Protection and Environment (Belgrade) and applied by a back sprayer (Solo, Germany) to apple and plum stocks; 1.5 L water solution of copper citrate was applied per plot (10 plants) at concentrations of 0.5%, 1.0%, 1.5% and 2.0%. Bordeaux mixture (2.0%) and urea (4.0%) were used as standards. Control nursery stocks were not treated. The experiment used a randomized block design, with 40 nursery stocks treated per each variant, 10 stocks in each of four repetitions. The trial was carried out on 18th October 2016, and on 14th September 2017. No other chemical compound was applied during trial, including a foliar fertilizer.

The results were evaluated three times every seven days from the moment of treatment and there were four ratings in total. The basic parameter in assessments was the leaf area affected by necrosis, which was rated on a scale from 0 to 4 (0 – without necrosis; 1 – necrosis covering 10% of leaf surface; 2 – necrosis covering 10-25% of leaf surface; 3 – necrosis covering 25-50% of leaf surface; 4 – necrosis covering more than 50% of leaf surface) (EPPO, 2014). Assessment of defoliation was rated on a scale from 0 to 4 (0 - without defoliation; 1 – defoliation < 10%; 2 – defoliation 10-25%; 3 – defoliation 25-50% and 4 – defoliation > 50%). Phytotoxicity and defoliation data were evaluated using Townsend-Heuberger's formula (Townsend & Heuberger, 1943). The results were processed by analysis of variance (ANOVA) with means separated by Tuckey's test ($P \leq 0.05\%$).

RESULTS AND DISCUSSION

The results of our study showed that copper citrate successfully contributed to defoliation of nursery fruit stocks. A difference in defoliation effects was noticed between stone and pome fruit stocks (Figure 1).

The data on phytotoxicity and degree of defoliation caused by different copper citrate concentrations and standard compounds used for that purpose in one year old apple stocks during 2016 and 2017 are summarized in Table 1.

The data on phytotoxicity and degree of defoliation of one year old plum stocks during 2017 are presented in Table 2.

Figure 1. Efficiency of defoliation of plum (a) and apple (b) stocks in nursery using copper citrate at 2% concentration

Table 1. Degrees of phytotoxicity to one year old apple stocks, and their defoliation in 2016 (Ljubava) and 2017 (Milutovac)

Treatment	Concentration	Degree of phytotoxicity (%)		Degree of defoliation (%)	
		2016	2017	2016	2017
Copper citrate	0.5%	23.8 cd	16.9 d	42.5 d	22.5 de
	1.0%	31.3 bcd	61.3 b	56.3 c	49.4 bc
	1.5%	45.0 abc	84.4 a	62.5 bc	65.6 ab
	2.0%	59.6 ab	95.6 a	64.4 bc	80.6 a
Bordeaux mixture	2.0%	75.6 a	42.5 c	71.3 a	51.3 bc
Urea	4.0%	75.6 a	37.5 c	75.0 ab	35.0 cd
Untreated	/	4.4 d	5.6 d	18.1 e	7.5 e

Means in columns marked by different letters differ significantly (P≤0.05; Tukey's multiple range test)

Table 2. Degrees of phytotoxicity to one year old plum stocks and their defoliation in 2017 (Milutovac)

Treatment	Concentration	Degree of phytotoxicity (%)	Degree of defoliation (%)
Copper citrate	0.5%	78.1 b	90.0 ab
	1.0%	97.5 a	100.0 a
	1.5%	100.0 a	100.0 a
	2.0%	100.0 a	100.0 a
Bordeaux mixture	2.0%	60.1 c	98.1 a
Urea	4.0%	73.1 b	78.1 b
Untreated	/	3.1 d	38.7 c

Means in columns marked by different letters differ significantly (P≤0.05; Tukey's multiple range test)

In the plum nursery, each applied concentration of copper citrate resulted in a high level of defoliation: its efficacy was 90% at the lowest concentration of 0.5%, while the defoliation level was 100% at concentrations of 1.0%, 1.5% and 2.0%. Treatment with Bordeaux mixture also showed a high level of defoliation (98.13%). A significantly lower, but still relatively high level of defoliation (78.13%) was observed on nursery plum stocks treated with urea. Defoliation level of untreated nursery plum stocks was 38.75%, which was significantly lower than on treated stocks. Treatments with copper citrate provided satisfactory defoliation results in 2017.

Necrosis occurred on treated leaves in the form of brown-gray necrotic spots which covered larger or smaller leaf surface, depending on concentration applied. Leaves expectedly fell off faster from the treated than from untreated nursery apple and plum stocks. It was also observed that treated leaves were mechanically removed more easily than leaves from untreated nursery stocks.

Copper is an essential metal for normal plant growth and development, although it is also potentially toxic (Yruela, 2005). Toxicity caused by copper is a rare phenomenon in horticulture. The most frequent symptoms on plants in terms of excessive copper concentrations are inadequate, obstructed shoot and root growth and vigour, while chlorosis also frequently appears on leaves (Rusjan, 2012). Plants grown in the presence of high Cu levels normally show reduced biomass and chlorotic symptoms (Yruela, 2005).

Copper citrate was less efficient as a defoliant on nursery apple than on nursery plum stocks, although satisfactory results were achieved by applying its higher concentrations. The 2% concentration of copper citrate resulted in the highest level of defoliation (80.6%) of apple stocks, which declined progressively with decreasing concentrations: in 2017 defoliation levels were 65.6%, 49.4% and only 22.5% at the concentrations of 1.5%, 1.0% and 0.5%, respectively. It was also observed that Bordeaux mixture had a significantly greater defoliation effect (51.3%) than urea (35.0%), which caused a significantly higher level of defoliation than the control (7.5%). According to the results, copper citrate proved to be an efficient defoliant for nursery fruit stock. Higher concentrations of copper citrate (2.0 and 1.5%) showed higher efficiency in 2017 in comparison with 2016. This may be the result of a more convenient timing of treatment in 2017. On the other side, the most convenient timing for standard treatments (Bordeaux mixture and urea) was the middle of October.

In 2017, nursery plum stocks were included in the investigation. Copper citrate caused 100% defoliation of nursery plum stocks when applied at the concentrations of 1.0%, 1.5% and 2.0%, while defoliation of nursery apple stocks by copper citrate concentrations of 0.5%, 1.0% and 1.5% had considerably lower effect. The results show that the optimum concentration of copper citrate for defoliation of apple stocks is 2.0% or higher, which will probably be a subject of further investigation. In comparison with the applied standards, i.e. Bordeaux mixture and urea, the efficiency of copper citrate in defoliation of nursery apple stocks was significantly higher. It is import to point out that bud necrosis or other negative effects were not observed on the treated nursery stocks.

Preparations with copper oxychloride, copper hydroxide, chelate copper and Bordeaux mixture have been used not only for phytopathogens control but also for defoliation of nursery fruit stocks (Tomlin, 2006). To our knowledge, copper citrate has not been used for that purpose so far.

The main problem with using copper compounds is their poor solubility in water (such as oxychloride), as well as their phytotoxicity when applied at the usual concentrations (van Assche & Clijsters, 1990; Marschner, 1995; Jamar & Lateur, 2007; Kurnik et al. 2011; Aleksić et al. 2012). At pH 7, copper citrate has slightly higher solubility than copper chloride, but its solubility is higher at pH>7. In addition, copper citrate does not exhibit a phytotoxic effect when applied at the prescribed concentrations. This compound is more biologically utilizable for plants than other copper compounds, while it retains its fungicidal effect (Tomlin, 2006).

When copper-based preparations (including copper citrate) are applied as defoliants they affect plants by causing leaf necrosis. This type of necrosis is very different in appearance from the necrosis caused by phytopathogenic agents. Depending on the applied concentration of copper ions, necrosis may affect a significant leaf surface (20-70%). Leaves fall off from nursery fruit stocks because of the phytotoxicity of copper compounds. Application of copper citrate for defoliation also greatly facilitates mechanical removal of leaves.

The efficiency of copper-based defoliants is in correlation with weather conditions. They are more phytotoxic in cold weather and under high air humidity (Team of editors, 2016).

The efficiency of copper citrate in defoliation of nursery fruit stocks significantly depends on the applied concentration. As this compound has proved to be phytotoxic only to leaves and not to fruit tree buds, it is recommended for use at higher concentrations. For evaluation of results it is of great importance to determine the optimum time of application, to monitor weather conditions at the time of application and to show any correlation between these two important factors. It was

not possible in the present study to use the experience of other researchers or compare results because scientific literature offers no relevant data about the application of this compound as a defoliant.

Investigation will be continued in the next vegetation season with higher concentrations of copper citrate (3.0 and 4.0%), especially on nursery apple stocks.

Based on this two-year investigation, and the physical and chemical characteristics and efficiency of copper citrate, we infer that it could be a new solution for defoliation of nursery pome and especially stone fruit stocks.

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Bakar citrat – defolijant u proizvodnji sadnica voćaka

REZIME

U radu su prikazani efekti defolijacije sadnica jabuke i šljive, primenom različitih koncentarcija bakar citrata, kao nove formulacije, i standardnih preparata koji se koriste u ove svrhe (bordovska čorba, urea). Ogledi su sprovedeni u regionu Trstenika (Ljubava i Milutovac), koji je centar rasadničke proizvodnje u Srbiji. Tretiranja su obavljena tokom 2016. i 2017. godine. Na osnovu dobijenih rezultata zaključeno je da bakar citrat pokazuje visok potencijal za upotrebu u svrhu defolijacije sadnica jabuke i šljive. Korišćene koncentracije ovog jedinjenja su pokazale veću efikasnost u primeni na sadnicama šljive nego na sadnicama jabuke. Najbolji rezultati u oba ogleda su zabeleženi sa maksimalno primenjenom koncentracijom (2%), dok efekat defolijacije na sadnicama jabuke opada sa smanjenjem koncentracije. Stepen defolijacije jabuke primenom bakar citrata u koncentraciji od 2% kretao se od 80,6% do 95,6%, a kod šljive čak 100%. Potvrđeno je i da uspešna defolijacija sadnica jabuke i šljive značajno zavisi od vremena aplikacije kao i meteoroloških uslova.

Ključne reči: Bakar; Defolijacija; Rasadnička proizvodnja; Sadnice voćaka