The effect of the type of preparation on the deposit of copper while spraying the winter oilseed rape

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The aim of the research was to determine the copper deposit volume on winter oilseed rape in three development phase (according to the BBCH scale: 12, 14 and 16). The experiment was performed in triplicate at the spraying speed of 0.86 m $s^{-1.}$ Two working fluids were used: foliar fertilizer Mikrovit Copper 80 and a nanocopper preparation, at the dose of 160 g Cu $ha^{-1.}$ The deposition treatment of the plants was conducted in the spraying chamber 'Aporo1' at two pressures (0.20 and 0.28 MPa), using two different types of flat fan nozzles. The dried rape plants were mineralized, and then, in order to determine the deposit, the Cu element concentration was measured using the spectrometer. The largest deposit of copper was obtained using the foliar fertilizer Mikrovit Copper 80 and using a double flat fan nozzle DF 120-02. The statistical analysis of the results of the study showed a significant effect of the type of liquid used on the value of copper deposit on winter oilseed rape plants.

Key words: spray deposit, nozzles, foliar fertilizer, mineralization, plant protection

Introduction

One of the basic conditions for effective and safe protection of crop plants, as well as foliar fertilization, is the selection of the suitable spraying technique. The deposit of plant protection products or foliar fertilizers should be done in a way that maximises the amount of active substance, which settles or enters the plant. The even distribution and level of deposit of the liquid used is affected, apart from the development phase of plants, by the liquid dose and type of applied nozzles (Świechowski et al. 2014). The effectiveness of the spraying procedure and the amount of loss of chemicals is also affected by the quality of spraying (Douzals 2012).

Foliar feeding is a very effective way to replenish nutrients in the plants. Using microelements from fertilizers applied directly to the plant, the effect is greater than in the case of soil fertilization. There is increasing number of reports in the literature regarding the use of nanocolloid compounds in agriculture as potentially more effective plant protection agents, growth regulators and artificial fertilizers (Sharon et al. 2010, Rai and Bai 2011, Sokół 2012). These are mainly laboratory tests that primarily concern storage longevity of harvested crops (Lu et al. 2010, Kim et al. 2012, Li et al. 2012, Grzegorzewska and Kowalska 2013). Unfortunately, there is no information on the use of nanocollide compounds for the protection and fertilization of crop plants, so the authors in their own studies on spraying winter oilseed rape used, among others, copper oxide nanoparticles.

The aim of the study was to determine the copper deposit volume for winter oilseed rape (for three studied development phases: 12, 14, 16 BBCH) using the copper spray in two different forms – contained in the foliar fertilizer Mikrovit Copper 80 and in the preparation based on the copper oxide nanoparticles. An additional aim was also to assess the impact of nozzle type and pressure on copper deposition on plants.

Materials and methods

The experiment was conducted in 2016 under greenhouse conditions, at the Institute of Soil Science and Plant Cultivation, National Research Institute, Department of Weed Science and Tillage Systems in Wroclaw (Poland), using the modified I generation phytotest (Sekutowski 2011). The study involved three independent series of experiments, with three replicates in each series. The DK Extrovert F1 variety of winter oilseed rape was used for the studies, which was sprayed in the following development phases: 12 BBCH (2 leaves), 14 BBCH (4 leaves),

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16 BBCH (6 leaves). Test plants (winter oilseed rape) were sown in 150 mm diameter pots on a specially prepared substrate, which was a mixture of peat (pH = 6.5) and sand with a 0.6–0.8 mm diameter in a 2:1 ratio. After 28 days, the rape plants reached their first development phase, BBCH 12, for treatment, and after another 10 days the spraying procedure was performed for the BBCH 14 phase and after another 8 days, the rape was sprayed in the BBCH 16 phase.

The spraying treatment was performed in a spraying chamber 'Aporo1', at a constant working speed of 0.86 m s-1 and two pressures of 0.20 and 0.28 MPa. Two standard nozzles were used for research: flat fan XR 110-02 and double flat fan DF 120-02, which nozzle spray flow was 0.65 l min-1 at a pressure of 0.20 MPa, and 0.79 l min -1 at a pressure of 0.28 MPa.The height of the nozzles from the sprayed plants was 0.5 m. Table 1 presents the results of droplet size measurements, determined by the volume median diameter (VMD) parameter, for both tested nozzles. The droplet size range suit to droplet categories, according to ANSI/ASAE Standard 572.1 (ASABE Standard 572.1 2009). The size of the drops produced by the nozzles was determined in a laboratory at the Industrial Institute of Agricultural Engineering in Poznań (Poland) using the Spraytec laser particle analyzer (Malvern Instruments). According to ANSI/ASAE Standard 572.1 (ASABE Standard 572.1 2009), the nozzles were classified as fine droplets at both operating pressures tested.

Table 1. Results of the droplet category for the tested nozzles at a pressure of 0.20 and 0.28 MPa, determined according to the ANSI/ASAE S572.1 (ASABE Standard 572.1 2009)

Nozzle	Pressure (MPa)	VMD(microns)	Droplet Category
DF 120-02	0.20	221.1	fine
DF 120-02	0.28	204.1	fine
XR 110-02	0.20	206.0	fine
XR 110-02	0.28	191.2	fine

VMD=Volume median diameter - a value where 50% of the total volume or mass of liquid sprayed is made of up droplets larger than this value, and 50% is made up of droplets smaller than this value

Two preparations were used as a spraying liquid: foliar fertilizer Mikrovit Copper 80 of the Intermag company and the preparation containing the copper oxide nanoparticles of the <50 nm size. Both preparations were applied at the dose of 160 g Cu ha^{-1}, and the applied water volumes and spraying pressures were as follows: 250 l of water per hectare at a pressure of 0.20 MPa and 300 l of water per hectare at a pressure of 0.28 MPa.

The sprayed rape plants in the individual development phases were cut 24h after the treatment. The plants were dried, crushed and weighed, then placed in Teflon HP 500 dishes and mineralized. Mineralization was performed with the "wet" microwaving technique using nitric acid (Ultra Pure grade, Sigma Aldrich, 69.0–70.0%). To each sample of the plant was added 5 ml of HNO_3 acid and next samples was mineralized in the microwave oven Mars 5 (CEM, USA). The Cu content was determined in the mineralized samples using the atomic absorption spectrometry method with the SpectrAA 220 device (Varina, Australia). The correctness of the assay was verified with the reference material ERM-CD281 Rye Grass. The results obtained were provided in milligrams per kilogram of dry matter.

The statistical analysis of the test results was performed using the Statistica 12.5 program. Because the dependent variable (deposit) is not subject to normal distribution within the investigated groups (nozzle, liquid, pressure), in order to assess the impact of individual factors on the liquid deposit on the rape plants at individual development phases, the non-parameter Mann-Witney U test was performed. The tests were carried out at the significance level $\alpha=0.05$.

Results

The analysis of Figures 1–3 shows that, regardless of the nozzle and pressure used in the experiment, higher values of deposit at all three development phases of rape were obtained using the foliar fertilizer Mikrovit Copper 80 compared to nanoparticle treatment. It was observed that the double flat fan nozzle DF 120-02, regardless of the pressure used for spraying, is characterised by a higher copper deposit from the foliar fertilizer Mikrovit Copper 80 on the winter oilseed rape plants compared to a flat fan nozzle XR 110-02. The highest values of copper deposit from the foliar fertilizer Mikrovit Copper 80 through the double flat fan nozzle DF 120-02 for each studied development phase were noted at the pressure of 0.28 MPa, these values were: 387.1 mg kg^{-1} (BBCH 12), 76.6 mg kg^{-1} (BBCH 14), 57.2 mg kg^{-1} (BBCH 16). Compared to the value of copper deposit from the foliar fertilizer Mikrovit Copper 80 on the winter oilseed rape plants at the pressure of 0.28MPa for the flat fan nozzle XR 110-02, the use of double flat fan nozzle DF 120-02 increased the deposit by 44% (BBCH 12), by 69% (BBCH 14) and by 92% (BBCH 16).

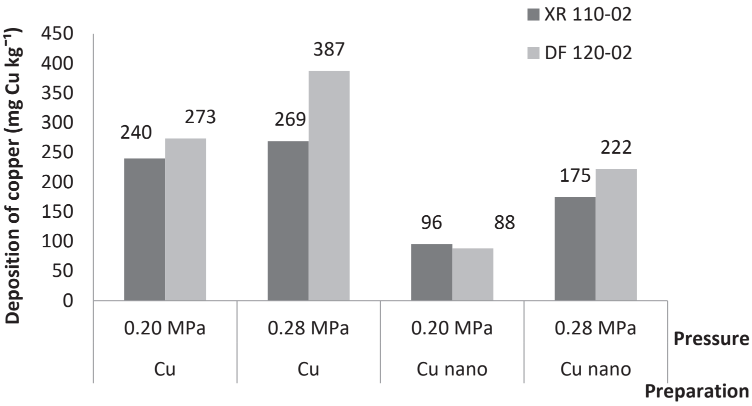

Fig.1. The deposit of copper to rape plants at the development phase of 2 leaves (12 BBCH) for the studied nozzles (flat fan XR 110-02 and double flat fan DF 120-02) at the pressure of 0.20 and 0.28 MPa. Cu –fertilizer was Mikrovit Copper 80 and Cu nano – contained nano copper.

The highest values of copper deposit from the preparation containing nanocollide particles were obtained for winter oilseed rape plants at the BBCH 12 development phase. The values of copper deposit from the nano copper applied at the pressure of 0.28 MPa were higher by 83% for the flat fan nozzle XR 110-02 and by 151% for the double flat fan nozzle DF 120-02 compared to the values obtained by applying nano copper at the pressure of 0.20 MPa. The lowest copper deposit values using nanopreparations were obtained during the spraying of rape plants at the BBCH 14 phase (Fig. 2), but the copper deposit increase was also observed at the development phase of the studied plants by 282% for the double flat fan nozzle DF 120-02 while increasing the pressure to 0.28 MPa.

Higher copper deposit values were observed when using nanopreparations for the flat fan nozzle XR 110-02 at the BBCH 12 phase by 8% and at the BBCH 14 phase by 87% compared to the double flat fan nozzle DF 120-02 operating at the pressure of 0.20 MPa. In other cases, regardless of the pressure, higher nonopreparation deposit values were noted using the double flat fan nozzle DF 120-02 for the treatment.

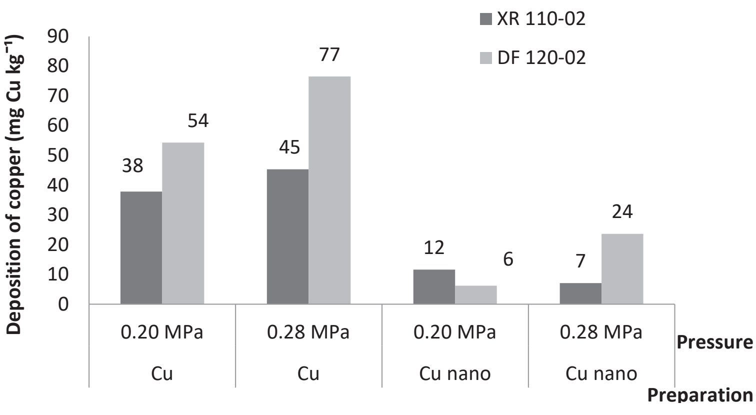

Fig.2. The deposit of copper on the rape plants at the development phase of 4 leaves (14 BBCH) for the studied nozzles (flat fan XR 110-02 and double flat fan DF 120-02) at the pressure of 0.20 and 0.28 MPa. Cu – fertilizer was Mikrovit Copper 80, and Cu nano – contained nano copper.

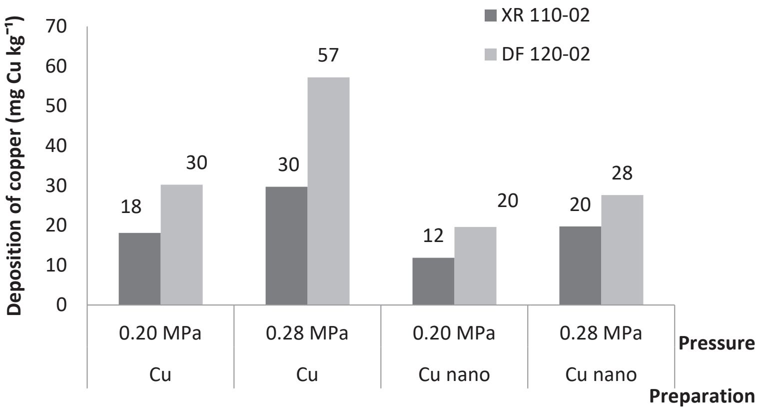

Fig.3. The deposit of copper on rape plants at the development phase of 6 leaves (16 BBCH) for the studied nozzles (flat fan XR 110-02 and double flat fan DF 120-02) at the pressure of 0.20 and 0.28 MPa. Cu – fertilizer was Mikrovit Copper 80, Cu nano – contained nano copper.

The results of the statistical analysis for individual development phases of rape plants are presented in Table 2. The impacts of the studied factors (independent variables) were also subjected to assessment, such as: nozzle, type of the liquid used and pressure, on the deposit values (dependent variable) of the liquid on the plants.

Based on the data analysis (Table 2) it can be stated that the selection of the type of nozzle for spraying the winter oilseed rape at the 12 and 14 development stages in the BBCH scale did not have a statistical impact on the value of copper marking value deposit contained in the liquids used in the studies.

Table 2. The results of Mann-Whitney U test for the studied development phases of winter oilseed rape

Development phase of rape	Factor	Deposition		
		Value statistics U	Value statistics Z	Value *p*
BBCH12	Nozzle	55.0000	0.9526	0.3408
	Kind the liquid spray	22.0000	2.8579	0.0043
	Pressure	33.0000	-2.2228	0.0262
BBCH14	Nozzle	52.0000	1.1258	0.2602
	Kind the liquid spray	0.0000	4.1280	0.0000
	Pressure	56.0000	-0.8949	0.3708
BBCH16	Nozzle	30.0000	2.3960	0.0166
	Kind the liquid spray	31.0000	2.3383	0.0194
	Pressure	29.0000	-2.4537	0.0141

In the development phase BBCH 14 of rape the pressure did not have a statistically significant effect on the copper deposit value on plants. While the statistically significant influence on the dependent variable (deposit) was noted for all studied development phases of winter oilseed rape plants in relation to the type of liquid used. The studied independent variable – pressure – had a statistically significant impact on the dependent variable – deposit at the development phase of rape BBCH12 and 16 at the significance level of $\alpha=0.05$.

Discussion

The deposit of the liquid on the plants is one of the main indicators determining the quality of spraying crops. The index of deposit is most commonly determined using the filter papers placed on plants (Raetano and Bauer 2003, Celen et al. 2009, De Souza Christovam et al. 2010ab, Sánchez-Hermosilla et al. 2012, Świechowski et al. 2012). The location of the samplers in order to determine the deposit of the studied liquid directly on the plants can cause measurement errors due to the loading of leaves with samplers. Therefore, the authors used the whole winter oilseed plants in their own studies to determine the deposit.

Various markers are used to evaluate the deposit, among others: BSF fluorescence (Brilliant Sulfaflavine), tartazine or nigrosine (Larsolle et al. 2002, Bayat and Bozdogan 2005, Balsari et al. 2007, Celen et al. 2009, Arvidsson et al. 2011, Świechowski et al. 2015). The metallic elements are another markers used to determine the deposit index. De Souza Christovam et al. (2010a) used copper oxychloride as a marker in their studies. Raetano and Bauer (2003) used copper oxide, while De Souza Christovam et al. (2010b) used a copper preparation called Cobox (50% of metallic copper). These authors marked the copper ion concentration in the studied samples using the atomic absorption method with spectrophotometer. Our study used the foliar Mikrovit Copper 80 fertilizer and copper oxide containing nanoparticles of the <50 nm size as the markers. The concentration of copper ions was determined similarly to the study by De Souza Christovam et al. (2010a and 2010b) with the method of wet digestion and AAS measurement. The analysis of the obtained results showed that the higher deposit values were obtained with the foliar fertilizer Mikrovit Copper 80 for all studied development phases of the rape plants. During the studies of the influence of the copper marker form on the level of deposit, the impact of parameters of the spraying process was also analysed, such as: pressure and type of nozzle on the obtained amount of deposit. Similar studies have been carried out by other researchers (Raetano and Bauer 2003, Świechowski et al. 2012).

De Souza Christovam et al. (2010a) in the study of liquid deposit on the soybean plants compared the impact of spraying techniques on the deposit of the spraying preparation on the filter papers. The flat fan nozzles XR 8002 and rotation nozzles LVO (low volume oily) were used for spraying, operating at different air speeds (0, 9 and 29 km h^{-1}) produced by the spray fan with auxiliary air flow. The authors have found that the air speed does not affect the amount of liquid applied on the leaf surface in the upper part of the soybean plants. While Raetano and Bauer (2003) carried out the deposit studies on the bean plants, with filter papers used as samplers placed in different parts of the plant. They investigated the effect of air speed (50, 75 and 100% of maximum yield) generated by the spray fan with an auxiliary air fan. According to their research, the use of an auxiliary air stream at the maximum speed, which is produced by the fan, results in the increased deposit of liquid on the lower surfaces of bean leaves. They also found that the statistical analysis did not show that the air speed differences affect the deposit of copper marker on the studied surfaces of bean plants.

Other researchers have investigated the effect of the nozzle type on the deposit of utility liquid in the crown of apple trees, in various phonological phases. Two types of nozzles were used in the studies: hollow cone TR 80-01 and air-injector ID 90-01. The authors have observed larger liquid deposit using hollow cone nozzles TR 80-01 (in the phase of establishment and full fruit formation) (Świechowski et al. 2012).

Two standard nozzles operating at different pressures were compared in this study. It was observed that the double flat fan nozzle DF 120-02 working at the pressure of 0.28 MPa was characterised with a higher deposit of utility liquid, compared to the flat fan nozzle XR 110-02. The highest values of the deposit of copper and nano copper marker were noted in the BBCH 12 phase of winter oilseed rape and ranged from 88.2 to 381.7 mg Cu kg^{-1} of dry matter. The lowest values of the copper deposit marker were noted while spraying the winter oilseed rape plants, which were at the development phase BBCH 16 and they ranged from 18.1 to 57.2 mg Cu kg^{-1} of dry matter, while the nano copper marker in the BBCH 14 phase, the lowest values ranged from 6.2 to 23.7 mg Cu kg^{-1} of dry matter.

The statistical analysis used showed the significant effect of the utility liquid type used for the spraying procedure on the value of copper marker deposit depending on the studied development phase of the winter oilseed rape plants.

Conclusions

1. Irrespective of the pressure used for the spraying procedure during the deposit of the double flat fan nozzle DF 120-02 the higher deposit of copper was obtained from the foliar fertilizer Mikrovit Copper 80 on the winter oilseed rape plants compared to the flat fan nozzle XR 110-02.

2. The largest deposit of copper was obtained using the foliar fertilizer Mikrovit Copper 80 for all development phases of winter oilseed rape (12, 14, 16 BBCH) and all spraying parameters used than with nanoparticle copper preparation.

3. At the pressure of 0.28 MPa, the use of a double flat fan nozzle DF 120-02 for spraying and the foliar fertilizer Mikrovit Copper 80 resulted in the increase of the deposit by 44% for the 12 BBCH phase, 69% for the 14 BBCH phase and 92% for the 16 BBCH phase compared to the flat fan nozzle XR 110-02.

4. Based on the results of the statistical analysis, a significant effect of the type of the utility liquid used for spraying winter oilseed rape in three studied development phases was stated on the deposit value. The foliar fertilizer Mikrovit Copper 80 was characterised by a better deposit compared to the preparation made using nano copper.

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