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EFFECT OF WATER HARDNESS AND SURFACTANT ON THE PARTICLE COVERAGE AND DISTRIBUTION OF PLANT PROTECTION PRODUCTS GRANULES

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Abstract

The paper presents a study done to determine how particles of different plant protection products (fungicides) are distributed onto treated surfaces when their solutions are prepared with water of different hardness and addition of surfactant. A total of fifteen plant protection products were studied, all in the same concentration of 0.3% with four type of solutions: only distilled water, distilled water plus a wetting agent – the organosilicone surfactant – Silwet L-77, very hard tap water (hardness = 196.9 ppm $CaCO_3$, 11 °dH) and very hard tap water plus wetting agent. The observations and images were made via light microscope with magnification 200X and 3MP digital camera. The images were analyzed for a percent distribution, and spreading of particles by ImageJ software. The results showed that the distribution, and coverage of particles onto treated surfaces can be different even at application of similar plant protection products. The variations in the properties were observed when the solutions were made with waters with different hardness and a wetting agent was added to the solutions. Contrary to the common perception that hard water can reduce the effectiveness of pesticides towards pests, according to the distribution and coverage of particles onto treated surfaces, in some cases hard water can even enhance these properties of the pesticide solutions.

Keywords: plant protection products, distribution, coverage, wetting agent, water hardness

INTRODUCTION

The low pesticide efficiency has caused serious environmental pollution and economic loss closely related to each link in the targeted delivery of pesticides (Bao et al, 2022). The even spreading and distribution of pesticides onto treated surfaces is extremely important for their effectiveness towards pests and also for their impact on the environment. The effective retention of pesticide droplets and particles on plant surfaces is an important challenge (Zheng et al., 2018). Spreading of agricultural sprays on plant surfaces is a significant task as it helps decrease the pesticide usage and thereby reduces the risk of environmental pollution (Song et al., 2020). The surfactant is an important additive in the pesticide application due to its antifoaming or foaming, buffering or stabilizing, sticking or wetting as well as its toxicity properties. The surfactant can lower the surface tension of the spray and enhance droplets deposition, spread, retention and phytotoxicity on plant surfaces (Appah et al., 2020). In aerial spraying tank-mix adjuvants are usually mixed with a pesticide solution to improve the efficiency of pesticides. Preventing pesticides from depositing in off-target areas is important in enhancing the pesticide utilization. Improving the wetting and spreading of pesticides is one of the most important ways to reduce pesticide droplets running off from the target (Meng et al., 2021). The conducted research shows that the effect of different formulations on the surface tension of the pesticide solution was not significant, but the effect of different adjuvants was significant and the same adjuvant showed different effects on different formulations (Bo et al., 2012). The fate of pesticide droplets on leaves is significantly influenced by the fine structures found on leaf surfaces (Yu et al., 2009) and the interaction between pesticide droplets and a leaf surface affects the deposition behavior of pesticides (He et al., 2021). The movement behavior of the droplet that impinges on the plant leaf surface is affected by many factors, among which the most important and the easiest to adjust are the spray droplet size and the impingement velocity (Li et al., 2021). Nevertheless, the use of appropriate tank-mix adjuvants at low dilution ratios can improve the performance of spray dilutions, increase the effective deposition and the wetting spread of pesticides on rice leaves, further reducing the dosage of pesticide products and improving pesticide utilization (Zhao et al., 2022). The conducted research with apple leaves found that the mean pesticide spray coverage on water-sensitive paper varied by up to 6.1% within an apple orchard, and the leaf residues varied by up to 0.95 mg/kg within a tree (Witton et al., 2018). Another research, revealed that the spray coverage on cotton plants varied, and, for both miticides, the significantly positive relationships between the spray coverage and the spider mite mortality were shown (Martini et al., 2012).

The research is about determining how the hardness of water and the addition of surfactants into treated solutions of the plant protection products affect the distribution and coverage of their particles onto surfaces.

MATERIALS AND METHODS

For the present investigation, a total of 15 plant protection products (fungicides) formulated as water dispersible powders WP or water dispersible granules WG were used, as follows:

- Bordo Mix 20 WG©: produced by IQV Agro; active substance: 20% w/w bordeaux mixture, formulation: Wettable powder (WP);
- Champion WP©: produced by Nufarm SAS, active substance: 50% w/w copper oxychloride, formulation: Wettable powder (WP);
- Cuprotsin Super M©: produced by Agria Bulgaria, active substance: 30% w/w copper oxychloride, 20% mancozeb, formulation: Wettable powder (WP);
- Curzate 60 WG©: produced by DuPont; active substance: 60% w/w cymoxanil; formulation: water-dispersible granulate (WG);
- Delan 70 WG©: produced by BASF; active substance: 70% w/w dithianon; formulation: water-dispersible granulate (WG);
- Equation Pro©: produced by DuPont; active substance: 22.1% w/w cymoxanil, 16.6% famoxadone; formulation: Wettable powder (WP);
- Funguran OH 50 WP©: produced by Spiess Urania Chemicals, active substance: 77% w/w copper hydroxide, formulation: Wettable powder (WP);
- Kabrio Top©: produced by BASF; active substance: 55% w/w metiram, 5% w/w pyraclostrobin; formulation: water-dispersible granulate (WG);
- Kumulus© DF: produced by BASF, active substance: 80% w/w sulfur, formulation: Water dispersible granule (WG);
- Manex©: produced by DuPont, active substance:37% w/w maneb, formulation: Wettable powder (WP);
- Melody Compact 49 WG©: produced by Bayer Crop Science, active substance: 8.4% w/w copper oxychloride, 40.6% w/w iprovalicarb; formulation: water-dispersible granulate (WG);
- Ridomil Gold R WG©: produced by Syngenta; active substance: 2% w/w metalaxyl-m, 14.1% w/w copper oxychloride; formulation: water-dispersible granulate (WG);
- Thiovit Jet©: produced by Syngenta, active substance: 80% w/w sulfur, formulation: Water dispersible granule (WG);
- Triomax WP©: produced by Agria, Bulgaria, active substances: 4% w/w

cymoxanil, 29% w/w copper oxychloride and 12% w/w mancozeb, formulation: Wettable powder (WP);

- Zato 50 WG©: produced by Bayer Crop Science; active substance: 50% w/w trifloxystrobin; formulation: water-dispersible granulate (WG)

All plant protection products were examined in the same concentration of 0.3% (w/v) in order to eliminate the concentration factor influence, and the solutions were prepared with:

- distilled water;
- distilled water plus 0.1% wetting agent (organosilicone surfactant for plant protection products – Silwet L-77© produced by Momentive Performance Materials Company GmbH Leverkusen, containing polyalkyleneoxide modified heptamethyltrisiloxane as a wetting agent substance);
- very hard tap water (hardness = 196.9 ppm $CaCO_3$, 11 °dH);
- very hard tap water plus 0.1% wetting agent (organosilicone surfactant for plant protection products – Silwet L-77©)

Standard microscopic slides (750 mm - 250 mm - 2 mm) were used and 1 ml of tested pesticide solution was sprayed via mini manual plastic trigger hand mist sprayer (300 ml volume tank capacity; 300 microns droplets size) onto it. One test variant consisted of 5 slides (replicates). After air drying of the solutions (in the thermostat at 20°C, for 24 hours), visual observations via a light microscope with magnification 200x were performed and images with 3MP digital camera were taken. One slide was pictured on three randomly selected places. This means that 15 images per variant were taken and analyzed. Images were processed for percent distribution and spreading of the particles by ImageJ software (https://imagej.net/ij/). ImageJ is a Java based open-source software extremely popular for analyzing images in the areas of biology, chemistry and technology (Abràmoff et al., 2004; Collins, 2007; Igathinathane et al., 2008). The using method for image processing was proved to be working in the area of measurement of pesticides spearing onto surfaces and accuracy of treatments (Mangado et al., 2013).

One-way ANOVAs statistical analyses were performed via R language for statistical computing for establishing the statistical proven differences between the variants (Ritz and Streibig, 2005; Teetor, 2011).

RESULTS AND DISCUSSION

The percentage coverage of the tested plant protection products solutions prepared with pure distilled water and distilled water plus organosilicone wetting agent are presented in Figures 1 and 2.

The results obtained show that different plant protection products can have a different distribution and coverage onto treated surfaces even though they are based on the same active substances. Kumulus DF and Thiovit Jet have 80% w/w sulfur as an active ingredient. However, their solutions prepared with distilled water have had different particles distribution and coverage - Kumulus DF achieved 35% better coverage compared to Thiovit Jet ($p<0.05$).

However, the addition of a wetting agent improved this property of Kumulus DF by approximately 20% ($p<0.05$) while Thiovit Jet showed no established significant differences ($p>0.05$). The organosilicone surfactant visually (with a naked eye) and significantly improved the spreading and wetting ability of solutions (established by K6 Force Tensiometer produced by KRÜSS GmbH) of all tested plant protection products onto slides.

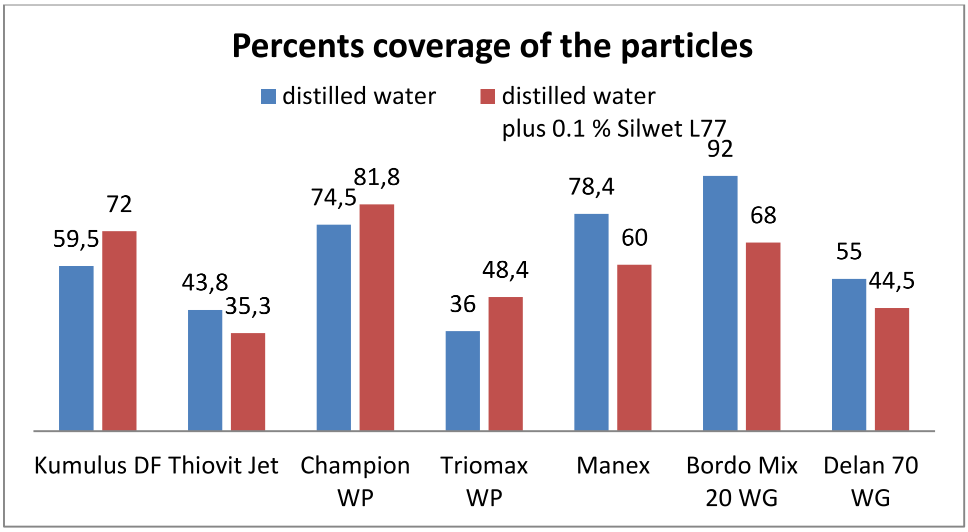

Figure 1. Percent of coverage of the particles with distilled water and distilled water plus organosilicone wetting agent

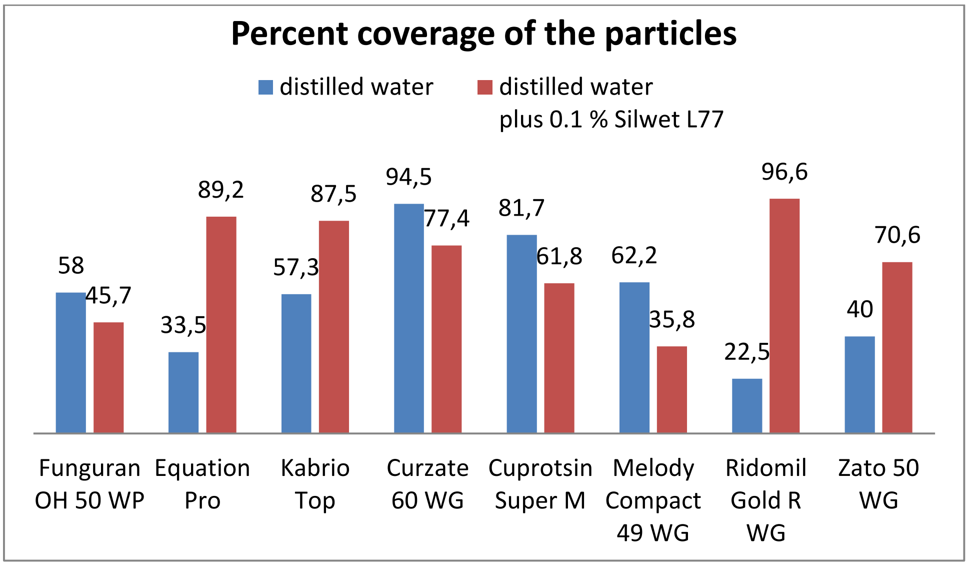

Figure 2. Percent of coverage of the particles with distilled water and distilled water plus organosilicone wetting agent

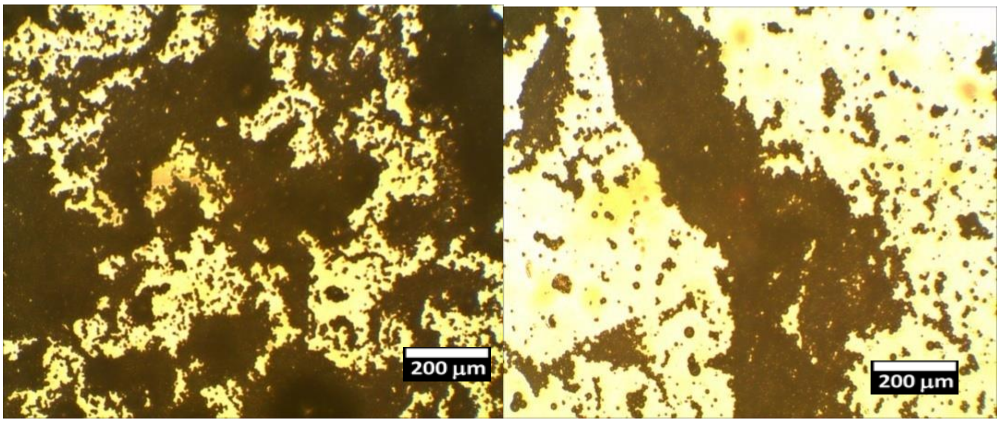

Figure 3. Solutions (0.3%) of Kumulus DF (left) and Thiovit Jet (right) prepared with distilled water

The microscopic images showed that the solutions of Champion WP, Triomax WP, Delan 70 WG, Fungoran OH 50 WP and Thiovit Jet prepared with distilled water did not have significant differences of particles distribution and coverage ($p>0.05$). In relation to other plant protection products such as: Equation Pr, Ridomil Gold R and Zato 50 WG, the improvement of particles distribution and coverage with the addition of a wetting agent was sizable ($p<0.05$) in the range of 330 -76.5%. From all tested fungicides Ridomil Gold R showed the lowest (22.5 %) while Bodo Mix 20 WG and Curzate 60 WG showed the highest (92% and 94.5%) particles distribution and coverage when their solutions were prepared with distilled water. However, the addition of a wetting agent to the solutions of Ridomil Gold R improved particles distribution and coverage in the highest degree.

Next Figures 5a and 5b. Percentage coverage of the fungicide particles in the experimental solutions done with very hard water.

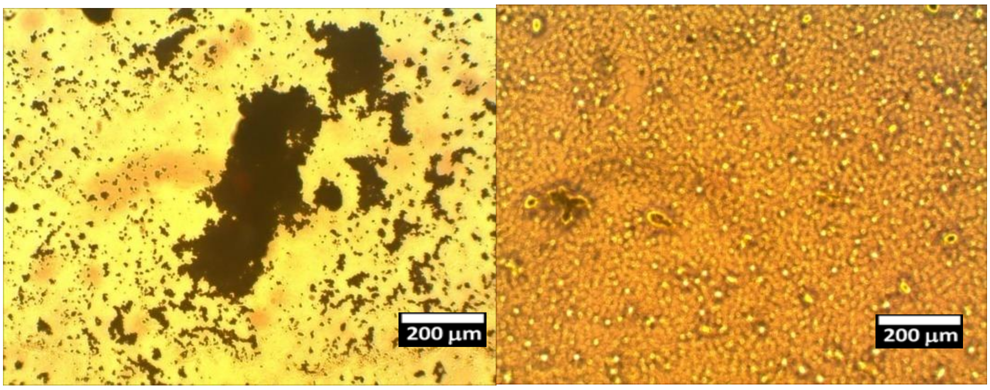

Figure 4. Ridomil Gold R – 0.3% solution prepared with distilled water (left) and solution prepared with distilled water plus organosilicone surfactant for plant protection products – Silwet L-77 (right)

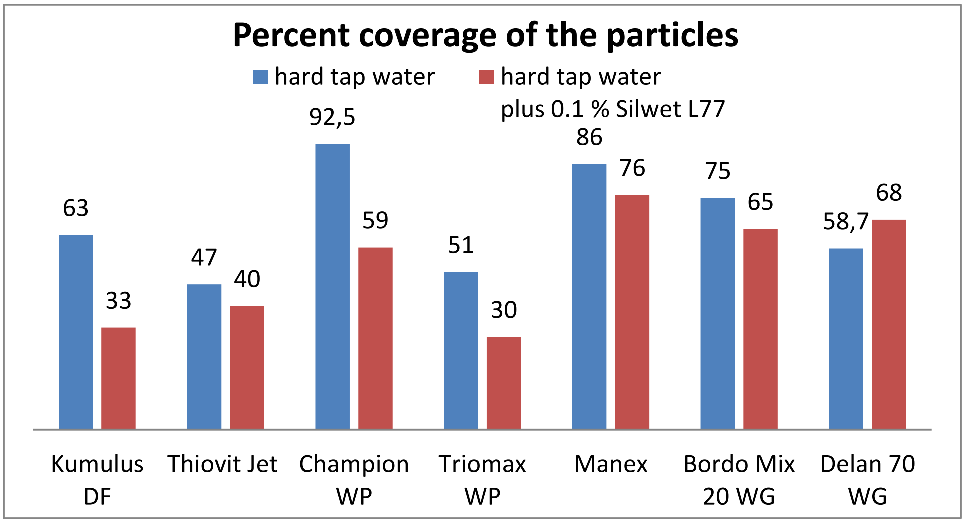

Figure 5a. Percent of coverage of the particles with very hard water and very hard water plus organosilicone wetting agent

The results show that using very hard water for preparations of the solutions did not affect the distribution and coverage of the particles of some of the products ($p>0.05$); however, towards others such as Champion WP, Triomax WP, Equation Pro and Zato 50 WG, the usage of very hard water actually increased the degree of distribution and coverage of the particles ($p<0.05$).

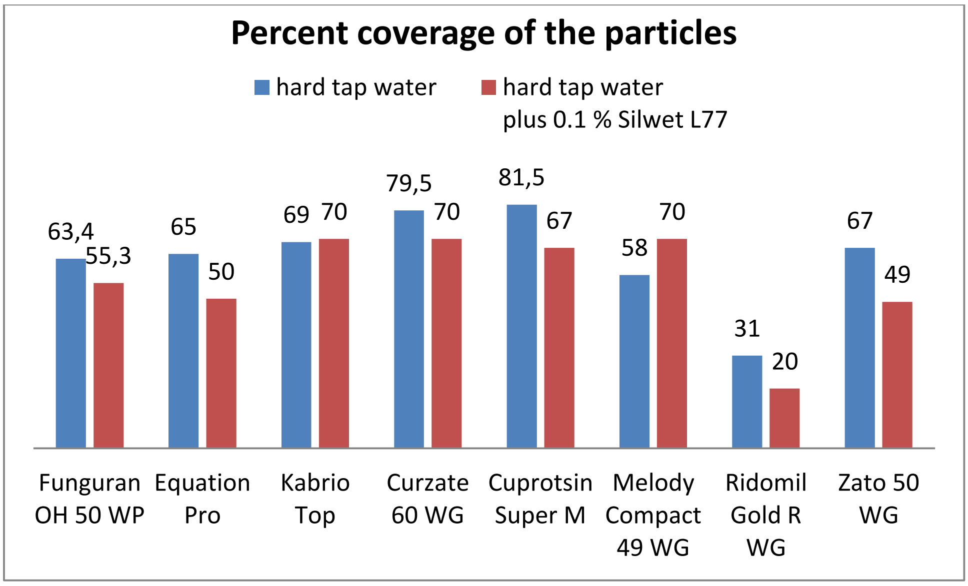

Figure 5b. Percent of coverage of the particles with very hard water and very hard water plus organosilicone wetting agent

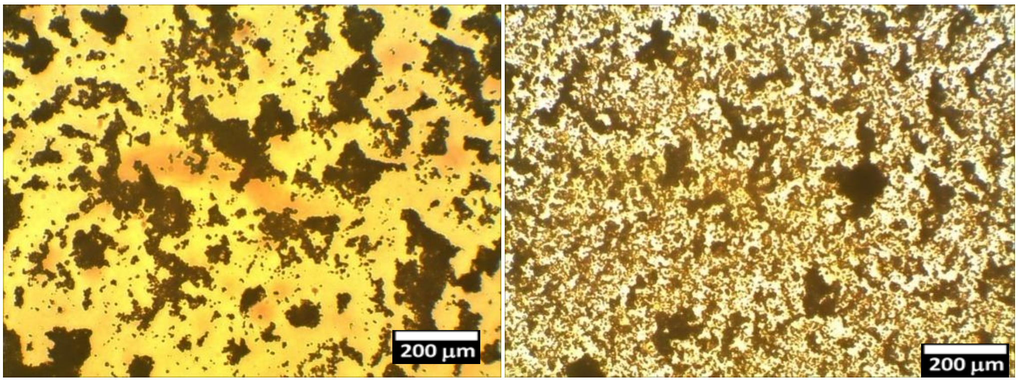

Figure 6. Zato 50 WG – 0.3% solution prepared with distilled water (left) and with very hard water (right)

An opposite effect was observed towards Bordo Mix 20 WG and Curzate 60 WG ($p<0.05$). The addition of the organosilicone wetting agent to the plant protection products solutions prepared with very hard water decreased the distribution and coverage of the particles towards Kumulus DF, Champion WP, Triomax WP, Cuprotsin Super M, Ridomil Gold R WG and Zato 50 WG, while towards Melody Compact 49 WG an increment was observed.

The method for using the microscope images for making an analysis of pesticide treatments, and pesticide particles onto treated with pesticide solution surfaces is not new (Hart, 1979). However, using the scanning electron microscope is a very expensive method, but mandatory if such research is conducted with leaves and other plant parts. By using simple microscopic glass slides and a common light microscope, the spreading and distribution of pesticide particles and the influence of wetting and sticky agents on this process can also be revealed at a much lower price and in a shorter period of time. The glass is a fully hydrophobic smooth surface. The use of real leaf surfaces in not appropriate due to the great variations in the texture and type of surfaces, and this will work only if the pesticides are applied in relatively high concentrations when the distribution and spreading of the particles can be detected via a stereo microscope. According to many studies, water hardness is one important property that can influence the performance of pesticides. By increasing the hardness of water, the performance of the plant protection products is reduced (Gupta et al., 2008; Schortgenand Patton, 2020; Ranjbar et al., 2021). However, the present study showed that the water hardness affects the distribution and coverage of particles for only two out of all 15 tested fungicides - Bordo Mix 20 WG (active substance: 20% w/w Bordeaux mixture) and Curzate 60 WG (60% w/w cymoxanil). In many investigations, the addition of wetting agents to the pesticides' solutions can increase their effectiveness significantly (Karnok et al., 2004; Czarnota and Thomas, 2010; Hazra and Purkait, 2019). In this study the addition of the organosilicone wetting agent improved the distribution and coverage of particles onto treated surfaces only for a few of the tested plant protection products - Ridomil Gold R WG (in a very big degree), and for Zato 50 WG, Kabrio Top and Equation Pro - when their solution was done with distilled water. Towards other pesticides such as Bordo Mix 20 WG, Curzate 60 WG, Cuprotsin Super M and Melody Compact 49 WG, the presence of the organosilicone wetting agent actually decreased the distribution and coverage of particles onto treated surfaces. The results were different when very hard water mixed with an organosilicone wetting agent was used.

CONCLUSION

The conducted investigation shows that the distribution and coverage of particles onto sprayed with pesticide solutions surfaces can vary even among very similar plant protection products such as Kumulus DF and Thiovit Jet. The better distribution and coverage will lead to a better exposition of pests to the pesticides and respectively – better effectiveness. Revealing this property can be important for choosing between the similar plant protection products like Kumulus DF and Thiovit Jet, for example. The research revealed that this property can vary when water with different hardness is used for the preparation of the pesticide solutions. Despite the common perception that hard water can reduce the effectiveness of pesticides towards pests, according to the distribution and coverage of particles onto treated surfaces, in some cases, hard water can even increase it. This is very important because, in many cases, farmers cannot use other sources of water for the preparation of their pesticide solutions. The other variant is to use hard water softeners ajuvants which of course will increase spraying costs. The addition of a wetting agent although strongly increases the spread of solutions onto sprayed surfaces, towards particles of the plant protection products can even reduce it. This also varies when water with different hardness is used for the preparation of solutions, so the additions of such kinds ajuvants is strongly recommended for achieving the best effectiveness from the pesticide spraying.

REFERENCES

Abràmoff, M. D., Magalhães, P. J., & Ram, S. J. (2004). Image processing with ImageJ. *Biophotonics international*, 11(7), 36-42

Appah, S., Jia, W., Ou, M., Wang, P., & Asante, E. A. (2020). Analysis of potential impaction and phytotoxicity of surfactant-plant surface interaction in pesticide application. *Crop Protection*, 127, 104961. https://doi.org/10.1016/j.cropro.2019.104961

Bao, Z., Wu, Y., Song, R., Gao, Y., Zhang, S., Zhao, K., & Du, F. (2022). The simple strategy to improve pesticide bioavailability and minimize environmental risk by effective and ecofriendly surfactants. *Science of The Total Environment*, 851, 158169.

https://doi.org/10.1016/j.scitotenv.2022.158169

Bo, W., Jianli, S., Aijun, Z., Yajia, L. I. U., Jing, Z. H. A. N. G., & Xiongkui, H. E. (2012). Effects of formulations and surfactants on the behavior of pesticide liquid spreading in the plant leaves. *农药学学报*, 14(3), 334-340.

Collins, T. J. (2007). ImageJ for microscopy. Biotechniques, 43(S1), S25-S30.

Czarnota, M., & Thomas, P. A. (2010). Using surfactants, wetting agents, and adjuvants in the greenhouse. *Bulletin*, 1314, University of Georgia

Gupta, A. K., Verma, G. P., & Jain, K. L. (2008). Acute toxicity of organophosphate insecticide, dichlorvos in relation to selected water hardness for the freshwater zooplankters. *Journal of Environmental Biology*, 29(6), 837-839.

Hart, C. A. (1979). Use of the scanning electron microscope and cathodoluminescence in studying the application of pesticides to plants. *Pesticide Science*, 10(4), 341-357. https://doi.org/10.1002/ps.2780100410

Hazra, D. K., & Purkait, A. (2019). Role of pesticide formulations for sustainable crop protection and environment management: A review. *Journal of Pharmacognosy and Phytochemistry*, 8(2), 686-693

He, L., Xi, S., Ding, L., Li, B., Mu, W., Li, P., & Liu, F. (2021). Regulating the entire journey of pesticide application on surfaces of hydrophobic leaves modified by pathogens at different growth stages. *ACS nano*, 16(1), 1318-1331. https://doi.org/10.1021/acsnano.1c09221

Igathinathane, C., Pordesimo, L. O., Columbus, E. P., Batchelor, W. D., & Methuku, S. R. (2008). Shape identification and particles size distribution from basic shape parameters using ImageJ. *Computers and electronics in agriculture*, 63(2), 168-182

Karnok, K. J., Xia, K., & Tucker, K. A. (2004). Wetting agents: What are they, and how do they work. *Golf Course Management*, 72(6), 84-86.

Li, H., Niu, X., Ding, L., Tahir, A. S., Guo, C., Chai, J., & Shang, Z. (2021). Dynamic spreading characteristics of droplet impinging soybean leaves. International *Journal of Agricultural and Biological Engineering*, 14(3), 32-45. https://doi.org/10.25165/j.ijabe.20211403.6274

Mangado, J., Arazuri, S., Arnal, P., Jarén, C., & López, A. (2013). Measuring the accuracy of a pesticide treatment by an image analyzer. *Procedia Technology*, 8, 498-502. https://doi.org/10.1016/j.protcy.2013.11.066

Martini, X., Kincy, N., & Nansen, C. (2012). Quantitative impact assessment of spray coverage and pest behavior on contact pesticide performance. *Pest management science*, 68(11), 1471-1477. https://doi.org/10.1002/ps.3330

Meng, Y., Wang, M., Wang, Z., Hu, H., & Ma, Y. (2021). Surface tension and spreading coefficient of single-and mix-pesticide solutions with aerial spraying organosilicone adjuvant. *International Journal of Precision Agricultural Aviation*, 4(1). https://doi.org/10.33440/j.ijpaa.20210401.159

Ranjbar, S., Allahyari, H., TalebiJahromi, K., & Heidari, A. (2021). The influence of water hardness and pH on the toxicity of insecticides on Bemisiatabaci. *Applied Entomology and Phytopathology*, 89(1), 103-115. https://doi.org/10.22092/jaep.2021.353652.1393

Ritz, C., & Streibig, J. C. (2005). Bioassay analysis using R. *Journal of statistical software*, 12, 1-22.

Schortgen, G. P., & Patton, A. J. (2020). Weed control by 2, 4-D dimethylamine depends on mixture water hardness and adjuvant inclusion but not spray solution storage time. *Weed technology*, 34(1), 107-116. https://doi.org/10.1017/wet.2019.117

Song, Q., Mei, L., Zhang, X., Xu, P., Dhinakaran, M. K., Li, H., & Yang, G. (2020). Spreading of benquitrione droplets on superhydrophobic leaves through pillar [5] arene-based host–guest chemistry. *Chemical Communications*, 56(55), 7593-7596. https://doi.org/10.1039/D0CC02187C

Teetor, P. (2011). R cookbook: Proven recipes for data analysis, statistics, and graphics. " O'Reilly Media, Inc.".

Witton, J. T., Pickering, M. D., Alvarez, T., Reed, M., Weyman, G., Hodson, M. E., & Ashauer, R. (2018). Quantifying pesticide deposits and spray patterns at micro-scales on apple (Malusdomesticus) leaves with a view to arthropod exposure. *Pest management science*, 74(12), 2884-2893. https://doi.org/10.1002/ps.5136

Yu, Y. A. N. G., Zhu, H., Frantz, J. M., Reding, M. E., Chan, K. C., & Ozkan, H. E. (2009). Evaporation and coverage area of pesticide droplets on hairy and waxy leaves. *Biosystems engineering*, 104(3), 324-334. https://doi.org/10.1016/j.biosystemseng.2009.08.006

Zhao, R., Sun, Z., Bird, N., Gu, Y. C., Xu, Y., Zhang, Z. H., & Wu, X. M. (2022). Effects of tank-mix adjuvants on physicochemical properties and dosage delivery at low dilution ratios for unmanned aerial vehicle application in paddy fields. *Pest Management Science*, 78(4), 1582-1593. https://doi.org/10.1002/ps.6777

Zheng, L., Cao, C., Cao, L., Chen, Z., Huang, Q., & Song, B. (2018). Bounce behavior and regulation of pesticide solution droplets on rice leaf surfaces. *Journal of agricultural and food chemistry*, 66(44), 11560-11568. https://doi.org/10.1021/acs.jafc.8b02619