Crop Protection 106 (2018) 50–57

Contents lists available at ScienceDirect

Crop Protection

journal homepage: www.elsevier.com/locate/cropro

Tank-mix of chlorantraniliprole and manganese foliar fertilizers: Impact on rheological characteristics, deposit properties and cuticular penetration

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ARTICLE INFO

Keywords:
Cuticle
Fertilizers
Mixtures
Organosilicone
Surface tension

ABSTRACT

The precise understanding of the interactions of adjuvants, agrochemicals and foliar fertilizers is essential to improve the efficacy of spray applications. In this study, we explored the influence of manganese foliar fertilizers (manganese sulfate and manganese nitrate) tank-mixed with an insecticide (chlorantraniliprole) and one organosilicone surfactant on the rheological properties of the solution, cuticular penetration and deposit characteristics on isolated tomato fruit cuticles. Higher $Mn(NO_3)_2$ concentrations induced higher contact angles and surface tensions whereas higher $MnSO_4$ concentrations induced only higher surface tension. The cuticular penetration (%) of $MnSO_4$ and $Mn(NO_3)_2$ were respectively 3% and 21% of the applied Mn amount. Addition of the organosilicone adjuvant significantly increased the cuticular penetration of both salts to 20% for $MnSO_4$ and 35% for $Mn(NO_3)_2$. Both manganese salts, when mixed in equal proportion, showed a penetration of 25%, which was not statistically different if adjuvant was added (23%). The foliar fertilizers did not influence cuticular penetration of chlorantraniliprole. Our results confirm the fact that many processes cannot be predicted for field applications. Thus, these model systems can be used to try to understand, and in a few situations to try to predict what could happen, and understand the behaviour and causal relations only.

1. Introduction

The use of agrochemicals to avoid or reduce pest and disease damage is of importance in order to ensure maximum yield under modern crop cultivation. The use of more than one product in the application tank is a common and important practice to affect more than one target (e.g. control of insects and foliar fertilization) and reduce the total number of applications, unnecessary environment contamination and the final production costs. According to a recent representative survey in more than 17 Brazilian federal states, 97% of the farmers practice tank mixture, while 95% of the spray solutions contain two to five different agrochemicals (Gazziero, 2015). When spraying pesticides containing synthetic active ingredients (a.i.), the tank-mixture of foliar fertilizers and adjuvants is common practice. In Brazil, the current practice in transgenic soybean, for example, is to prepare spray solutions containing three or four active ingredients (herbicide, insecticide, fungicide) mixed with foliar fertilizer and at least one adjuvant.

It is common knowledge that specific a.i.s have to stay on the leaf surface after application, while others have to reach the interior of the plant tissue, in order to deploy them expected biological activities. This aspect as well as many other properties of the a. i. are considered in the development and registration of new commercial products. However, the mixture of different products in the application tank might induce alterations in the physicochemical characteristics of the final spray solution. With this, direct and indirect effects on a.i. absorption might arise, posing a risk to the expected bio-efficacy (Cunha and Alves, 2009).

Salts are hygroscopic and may remain deliquescent (liquid) on the leaf surface after evaporation of visible water, due to the elevated humidity within the leaf boundary layer coming from stomatal transpiration (Burkhardt et al., 1999; Burkhardt and Hunsche, 2013). The remaining solutions are highly concentrated and have ion-specific physicochemical properties, e.g. on the surface tension (Burkhardt et al., 2012; Zeng et al., 2015). Alterations of the physicochemical properties of the spray solution might also induce changes in the droplet deposition pattern on leaf surface (Basi et al., 2012), and influence

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https://doi.org/10.1016/j.cropro.2017.12.011
Received 18 August 2017; Received in revised form 8 December 2017; Accepted 10 December 2017

the a.i. distribution inside the droplet residue area (Hunsche and Noga, 2011). These factors may have a decisive impact on the cuticular penetration, often considered the most important path for the movement of externally applied products to the interior of the leaves. Stomatal uptake, however, can also be relevant, particularly when the superficial tension of the solution is lower than 30 mN m^{-1}, or the hydraulic activation of stomata was successful (Burkhardt, 2010).

Besides the common practice of having tank-mixtures of different compounds, there is little evidence about the impact on key parameters as related to spray quality (e.g. droplet size distribution), distribution of droplets and active ingredients on the leaf surface, penetration and biological efficacy. The same situation applies to the a.i. chlorantraniliprole, a widely used insecticide in tank mixtures to protect crops against major agricultural pests e.g. from the orders Lepidoptera, Coleoptera, Diptera, Isoptera and Hemiptera. This a.i. belongs to the group of diamides, and has low toxicity to mammals, birds, aquatic animals and natural enemies of insect pests (Brugger et al., 2010).

With the background that chlorantraniliprole is commonly tank-mixed with foliar fertilizers, we chose this active ingredient as a model compound. Our objective was to run a series of experiments to evaluate the impact of mixtures with manganese fertilizers on the physicochemical behavior of the spray solution, deposit properties on the plant surface, and cuticular penetration of both insecticide and the micronutrient fertilizer. Our working hypothesis is that the manganese fertilizers do not change the rheological properties of the treatment solution, but reduce the cuticular penetration of chlorantraniliprole. With this study, we open a new scientific chapter aiming at better understanding of the interactions between compounds in the tank mixture, in support of a target-oriented and efficacy-focused adoption of agrochemicals and foliar fertilizers in tank-mixtures.

2. Material and methods

2.1. Cuticular membranes

The studies were conducted under controlled conditions at the Institute of Crop Science and Resource Conservation (INRES), Horticultural Sciences, University of Bonn, Germany. Tomato plants (*Lycopersicon esculentum* Mill) of the cultivar Capricia (Rijk Zwaan Welver GmbH, Germany) were grown without any application of pesticides or foliar fertilizers in a commercial-like greenhouse at the experimental station Campus Klein-Altendorf (University of Bonn, Meckenheim, Germany). Sampling of fruits and isolation of cuticles was done as described elsewhere (Hunsche and Noga, 2008). Fully-ripe fruits were carefully harvested, transported to the lab, selected and used for the enzymatic isolation of the cuticular membranes. Disks (25 mm diameter) were punched out from the fruits with a cork borer. Cuticular membranes were enzymatically isolated using cellulase (20 mL L^{-1} Celluclast, National Centre for Biotechnology Education, The University of Reading, Reading, UK) and pectinase (20 mL L^{-1} Trenolin® Flot DF, Erbsloeh Geisenheim AG, Geisenheim, Germany), 14.7 g L^{-1} tri-Sodium citrate-dihydrate and 0.068 g L^{-1} NaN_3 (Sodium azide) for preventing microbial growth. The pH of the enzymatic solution was regulated to a range between 3.5 and 4. The solution was changed after seven days; thereafter, a new solution was prepared every 10–14 days. After approximately 50 days, when cuticles were completely free from cell walls, cuticular membranes were rinsed with distilled water and transferred into a Borax-buffer solution (pH = 9) for stopping enzyme activities, and stored in this buffer solution for another five days. Thereafter, cuticles were removed from the buffer solution, washed with distilled and deionized water, and dried at room temperature for two days before dry-storing in closed Petri dishes. Before each experiment, cuticles were checked for their integrity using a stereo microscope.

2.2. First experiment–rheological properties of Mn salt solutions: impact of salt concentration

Solutions were prepared with two manganese salts, Manganese sulfate ($MnSO_4.H_2O$, mol. weight 169.02 g mol^{-1}, Aldrich Chemistry) and Manganese Nitrate ($MnN_2O_6.xH_2O$, mol. weight 178.95 g mol^{-1}, Aldrich Chemistry), in a concentration range until the saturation point (Manganese sulfate - 4 M; Manganese nitrate – 20 M). Accordingly, concentration series for Manganese Sulfate (MS) was: 1 M, 2 M, 3 M and 4 M; concentration series for Manganese nitrate (MN) was: 1 M, 5 M, 10 M, 15 M and 20 M.

Surface tension (ST; n = 10 droplets) was determined using the pendant drop method (IFT) and expressed in mN m^{-1}. The static contact angle (CA) was measured on both left and right-side of a sessile 1 μL droplet placed on isolated tomato fruit cuticles (n = 10 droplets). Both CA and ST were determined with a droplet shape analysis system (DSA 30E, Krüss GmbH, Hamburg, Germany). The density of each solution was considered for the determination of the surface tension.

2.3. Second experiment – rheological properties and cuticular penetration of Mn: impact of an organosilicone surfactant

Treatment solutions were prepared with two manganese salts, Manganese sulfate ($MnSO_4.H_20$, mol. weight 169.02 g mol^{-1}, Aldrich Chemistry) and Manganese Nitrate ($MnN_2O_6.xH_2O$, mol. weight 178.95 g mol^{-1}, Aldrich Chemistry), the mixture of both, and one treatment containing a commercial surfactant (polyether trisiloxane-based super spreader 100% non-ionic, Break-Thru® S240 – BTS240). The treatments were done by a combination of each solutions with different concentrations as described in Table 1. Surface tension and Contact angle evaluations were done as described for experiment 1. The cuticular penetration was determined using the finite-dose system by quantifying the amount of penetrated Mn after a predefined time, according to the methodology previously described (Alexander and Hunsche, 2016; Kraemer et al., 2009). For this purpose, five 1 μL droplets were gently deposited on the cuticles (n = 8 for each treatment solution) with a Hamilton micro pipette (Hamilton Bonaduz AG, Hamilton, Switzerland). Immediately after application, the finite-dose penetration chambers were allocated inside a 0.15 cm^3 Perspex chamber which was kept under laboratory conditions.

The predefined penetration time was 48 h. On average, relative humidity was higher than 90%. After the penetration time, the cuticles were removed from the penetration chamber; the receiver solution was transferred to volumetric flasks (2 mL), which were filled up with distilled water. As reference, the treatment solutions were applied directly into the volumetric flasks (5 × 1 μL solution droplets) establishing the positive control (100% penetration). All samples were analyzed by atomic absorption spectrometry (AAS, PerkinElmer, Analyst 300, Wellesley, MA, USA) and the cuticular penetration was expressed as μg

Table 1
Manganese salts and organosilicone adjuvant in different concentrations.

Treatments	Salt Concentration (M)	Adjuvant Concentration (%)
$MnSO_4$	0.05	–
$Mn(NO_3)_2$	0.05	–
Mix	0.025 + 0.025	–
BTS240	–	0.05
BTS240 + $MnSO_4$	0.05	0.05
BTS240 + $Mn(NO_3)_2$	0.05	0.05
BTS240 + Mix	0.025 + 0.025	0.05
BTS240	–	0.5
BTS240 + $MnSO_4$	0.05	0.5
BTS240 + $Mn(NO_3)_2$	0.05	0.5
BTS240 + Mix	0.025 + 0.025	0.5