CÉSAR HENRIQUE SOUZA ZANDONADI

TANK MIXTURE OF PESTICIDES AND THEIR EFFECT OVER PEST CONTROL

Tese apresentada à Universidade Federal de Uberlândia, como parte das exigências do Programa de Pós-graduação em Agronomia – Doutorado, área de concentração em Fitotecnia, para obtenção do título de “Doutor”.

Orientador

Prof. Dr. João Paulo Arantes Rodrigues da Cunha

UBERLÂNDIA
MINAS GERAIS – BRASIL
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“Veni, Vidi, Vici
Vim, Vi, Venci.”

Caio Júlio César

*“*Debaixo do céu há um momento para tudo,
e tempo certo para cada coisa.”

Eclesiastes 3:1

Dedico,

Aos meus pais, Pedro e Lúcia e aos meus avós Lurdes e Orozimbo, que sempre guiaram minhas decisões ao longo de toda minha vida.

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SUMÁRIO

ABSTRACT

ZANDONADI, CÉSAR HENRIQUE SOUZA. Tank mixture of pesticides and their effect over pest control. 2019. 71 p. Thesis (Doctorate in Agronomy/Crop Science) – Federal University of Uberlândia, Uberlândia[1].

The use of different phytosanitary products aimed at reducing the damages caused by pests, diseases and nutritional deficiencies are of extreme importance to enhance the crops yield in field. The objective of this thesis was to evaluate the interaction between the tank mix of an organosilicon adjuvant, manganese foliar fertilizers and different insecticidal active ingredients on the physical-chemical characteristics and the active efficacy. The thesis was carried out in three complementary stages, the first being held at the University of Bonn in Germany and the last two at the Federal University of Uberlândia (UFU). In the first stage, the experiment was conducted to evaluate the influence of the organosilicon adjuvant on the cuticular penetration of chlorantraniliprole active and foliar fertilizers based on manganese (nitrate and sulphate). In the second stage the effect of the previous mixtures at the field level was evaluated at “Glória” experimental farm in Uberlândia, evaluating the effect of the mixture on the insecticide efficacy on the main pests in the tomato crop, as well as the effects on plant physiology and on the physical-chemical characteristics of the spray. In the third stage, which was carried out at “Água Limpa” experimental farm in Uberlândia, the effect of the mixture of foliar fertilizer based on manganese sulphate and organosilicon adjuvant on the efficacy of imidacloprid insecticide in guava crop was evaluated, as well as the effects of these mixtures in the physical-chemical characteristics of the spray. We observed in the first stage that the mixture of pesticides with foliar fertilizers and adjuvants is a very complex issue, while the result is, in most cases, little predictable under practical conditions. The physical-chemical evaluations changed according to each manganese salt added in the mixture. In the second stage, chlorantraniliprole showed efficacy and the mixture with manganese foliar fertilizers does not influence the efficacy of the insecticide nor the physiological characteristics of the plant. The addition of foliar fertilizer in the mixture reduced the pH and surface tension and increased the electrical conductivity and viscosity of the insecticidal solutions. In the third step we have that the organosilicon adjuvant reduced the surface tension and increased the viscosity and the pH. The number of nymphs and the level of infestation decreased with the treatments. The tank mix of organosilicon adjuvant and manganese foliar fertilizer did not influence the efficacy of the insecticide. We conclude that no change in the insecticide efficacy was observed in the evaluated experiments and regarding to the physical-chemical characteristics of the solutions, we observed that the addition of manganese foliar fertilizers and also the organosilicon adjuvant alter these characteristics.

Keywords: cuticular penetration; organosilicon adjuvant; imidacloprid; chlorantraniliprole; tomato; guava; physical-chemical characteristics; effectiveness; manganese sulphate; manganese nitrate; scanning electron microscope (SEM)

[1]Advisor: João Paulo A. R. da Cunha – UFU

RESUMO

ZANDONADI, CÉSAR HENRIQUE SOUZA. Mistura em tanque de produtos fitossanitários e seu efeito no controle de pragas. 2019. 71 f. Tese (Doutorado em Agronomia/Fitotecnia) – Universidade Federal de Uberlândia, Uberlândia[1].

O uso de diferentes produtos fitossanitários visando a redução de perdas causadas por pragas, doenças e mesmo por deficiências nutricionais é de extrema importância para que se obtenha máxima produtividade das culturas no campo. O objetivo dessa tese foi avaliar a interação entre a mistura de tanque de um adjuvante organosiliconado, fertilizantes foliares a base de manganês e diferentes ingredientes ativos inseticidas sobre características físico químicas da calda e a eficácia do ativo. A tese foi realizada em 3 etapas complementares, sendo a primeira realizada na Universidade de Bonn na Alemanha e as duas últimas na Universidade Federal de Uberlândia (UFU). Na primeira etapa, o experimento foi conduzido com o intuito de avaliar a influência do adjuvante organosiliconado na penetração cuticular do ativo clorantraniliprole e de fertilizantes foliares a base de manganês (nitrato e sulfato). Na segunda etapa, foi avaliado o efeito das misturas anteriores a nível de campo, na Fazenda experimental do Glória em Uberlândia, sendo avaliado o efeito da mistura sobre a eficácia de controle do inseticida sobre as principais pragas na cultura do tomate, assim como efeitos na fisiologia da planta e nas características físico químicas da calda. Na terceira etapa, que foi realizada na fazenda experimental Água Limpa em Uberlândia, foi avaliado o efeito da mistura de fertilizante foliar a base de sulfato de manganês e adjuvante organosiliconado sobre a eficácia de controle do inseticida imidacloprido na cultura da goiaba, assim como os efeitos dessas misturas nas características físico-químicas da calda. Observou-se que na primeira etapa a mistura de defensivos agrícolas com fertilizantes foliares e adjuvantes é um tema muito complexo, enquanto o resultado é, na maioria dos casos, pouco previsível sob condições práticas. As avaliações físico-químicas mudaram de acordo com cada sal de manganês adicionado na mistura. Na segunda etapa, o clorantraniliprole apresentou eficácia de controle e a mistura com fertilizantes foliares de manganês não influencia a eficácia do mesmo e nem as características fisiológicas da planta. A adição de fertilizante foliar na mistura reduziu o pH e a tensão superficial e aumentou a condutividade elétrica e a viscosidade das soluções inseticidas. Em relação a terceira etapa, o adjuvante organosiliconado reduziu a tensão superficial e aumentou a viscosidade e o pH. O número de ninfas e o nível de infestação diminuíram com aplicações dos tratamentos. A mistura em tanque de adjuvante organosiliconado e fertilizante foliar manganês não influenciou o nível de eficácia do inseticida. Concluiu-se que, não há alteração na eficácia de controle do ativo inseticida nos experimentos avaliados e em relação as características físico químicas da calda; e a adição de fertilizantes foliares a base de manganês e também do adjuvante organosiliconado alteram essas características.

Palavras-chave: penetração cuticular; adjuvante organosiliconado; imidacloprido; clorantraniliprole; tomate; goiaba; características físico químicas; eficácia controle; sulfato de manganês; nitrato de manganês; microscópio eletrônico de varredura (SEM);

[1]Orientador: João Paulo A. R. da Cunha - UFU

CHAPTER I: TANK MIXTURE OF PESTICIDES AND THEIR EFFECTS OVER APPLICATION TECNOLOGY AND EFFICACY

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1 INTRODUCTION

The farms system around the world are more sustainable than years ago; growers had to work in a way that they should use only the necessary resources to produce in equal quantity or even more (in the same area) using less resources than before, respecting the environment and being socially fair. This kind of system has an impact in different areas inside the farm, since differences in soil cultivation to more efficient ways to use chemical products to enhance production.

Brazil is nowadays one of the countries that produce more food with less use of pesticide. In comparison to 20 other important producer countries, Brazil is the 13^{th} in use of pesticide (US$) per amount of produced product (ton) using less than 10 US$ per ton of product produced. The other counties are, Japan (100 US$ per ton) – 1^{st}; Germany and France (25 US$ per ton) 4^{th} and 5^{th} and USA with more than 10 US$ dollar (Sindiveg, 2018). According to the National Union of the Plant Protection Industry – SINDIVEG – the use of pesticides (US dollar) per area (hectare) in these countries are: Japan (1^{st} position) US$ 1200.00 per ha; Germany (2^{nd} position) 200 US$ per ha and Brazil (7^{th} position) with less than US$ 200 ha^{-1}(Sindiveg, 2018).

One remarkable practice among all growers around the word is the tank mixture of chemical products (mainly pesticides, adjuvants, and foliar fertilizers). This is a good application strategy, saving fuel and labor-hours, causing less soil compaction, and possibly providing a larger control of pest, diseases, nutritional deficiencies and weeds, aiming more efficacy, when compared to single product application (Tornisielo et al., 2013).

The tank mixture practice is common in Brazil and according to a survey made with Brazilian farmers from more than 17 states, about 97% of these farmers do tank mixture, being the mixture mostly (95%) made with 2 to 5 different products (Gazziero, 2015). Actually, in Brazil there is a law decree 4074/02 (Brasil, 2002) that regulate the use of pesticide, among other things. In October 2018, normative instruction 40 (Brazil, 2018) was approved and attributes to the agronomist engineer the responsibility for pesticide agronomic prescription, until this, the prescription could only reproduce the information contained in the pesticide label

In other countries for example, in European union (EU), to authorize some tank mixture, the products must present some tests, like tests of compatibility with other plant protection products (those plant protection products or adjuvant must be physically and chemically compatible in the tank mix) as well as biological compatibility. However, each country could legislate over this regulation. The mixing partners in a tank mixture from another EU Member State which has been authorized by mutual recognition must also be authorized or approved in Germany, for example (Tank Mixture Germany, 2015). This practice is common also in Australia, Canada, the U.S.A and the United Kingdom, where there are recommendations on application procedures, incompatibilities, and safety instructions (Tornisielo et al., 2013).

Knowing the chemical's mode of action is important to understand how the products are going to act in the mixture. In general, if the compounds present different mode of action they may not exhibit interaction at all (Lydy et al. 2004). One common mixture is the application of pesticides plus adjuvant.

The adjuvant concept is a product that enhances the active ingredient action and do not present any biological effect (Hazen, 2000). These products had influence in physical-chemical characteristics of the sprayed solutions, assisting the performance of the pesticides in adverse, environmental or mechanical conditions (Cunha, Alves e Reis, 2010; Kissman, 1998). To select the adjuvant, besides their physical-chemical characteristics, it should be taken into consideration the recommendations to each specific situation and the study of the effect of them in the interaction between the sprayed solution and the leaf surface. The adjuvant added to the mixture to enhance the efficiency acts in different ways. They could improve spreading of the droplet and the wetting of the spray mixture over the target (Cunha, Bueno and Ferreira 2010), as well as influence the penetration through the cuticle (Wang and Liu, 2007). Depending of the adjuvant composition and formulation, they could affect physical-chemical characteristics, mainly pH, surface tension and viscosity (Cunha and Alves, 2009).

In general, there are a lack of knowledge about some chemical products mode of action and if the efficiency of them compromised due to the possibility of negative interactions between the adjuvant and the pesticides, for example (Putti et al., 2014).

Other products that is commonly used in tank mixture are the foliar fertilizers. There are many processes involved, which make difficult the development of new strategies to optimize the efficiency of foliar sprays under different growing conditions and diverse plant species (Fernandez and Eichart, 2009). Ions like Fe^{3+} and Al^{3+} could react in tank mixtures with insecticides and fungicides (Petter et al., 2013), and also with insecticides and herbicides (Petter et al., 2012), changing some physical-chemical characteristics as well as reducing their efficacy (Pazzini et al. 2017; Ramos and Araujo, 2006).

Some of these fertilizers have in their composition some salts. These salts are hygroscopic and could stay over the leaf surface after water evaporation (Burkhardt et al., 1999; Burkhardt and Hunsche, 2013) and become highly concentrated and present some ion-specific physical-chemical properties, e.g. on the surface tension (Zeng et al., 2015; Burkhardt et al., 2012).

The tank mixture of chemical products could induce differences in plant physiology, in penetration of products though the cuticle (Melo et al., 2015; Alexander and Hunsche, 2016), droplet deposition pattern on leaf surface (Basi et al., 2012) or in physical-chemical characteristics of the sprayed solution (Cunha et al., 2010; Cunha and Alves, 2009).

Therefore, farmers have interest in receiving more accurate information about tank mixture, because the information available through a private service or through cooperatives are, according to the farmers, inadequate or inaccurate (Gazziero, 2015).

2 OBJECTIVES

2.1 General Objectives

Evaluate the interaction between the tank mixture of organosilicon adjuvant and manganese foliar fertilizers with different insecticides active ingredients over physical-chemical characteristics, penetration through the cuticle and effectiveness of the insecticides.

2.2 Specific Objectives

- Evaluate the impact of mixtures with manganese fertilizers and organosilicon adjuvant on physical-chemical properties of the spray solutions;
- Visualize the deposit properties on the plant surface;
- Quantify the cuticular penetration of both insecticide and manganese fertilizer.
- Evaluate the influence of manganese foliar fertilizers on the efficacy of the insecticide chlorantraniliprole over *Tuta absoluta* and *Neoleucinodes elegantalis* in the tomato crop;
- Evaluate the effects of these mixtures on tomato physiology;
- Evaluate the effect on the imidacloprid insecticide efficacy over *Triozoida limbata* control in guava trees.

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CHAPTER II - TANK-MIX OF CHLORANTRANILIPROLE AND MANGANESE FOLIAR FERTILIZERS: IMPACT ON RHEOLOGICAL CHARACTERISTICS, DEPOSIT PROPERTIES AND CUTICULAR PENETRATION [3]

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TANK-MIX OF CHLORANTRANILIPROLE AND MANGANESE FOLIAR FERTILIZERS: IMPACT ON RHEOLOGICAL CHARACTERISTICS, DEPOSIT PROPERTIES AND CUTICULAR PENETRATION

SUMMARY

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.

Keywords: cuticle, fertilizers, mixtures, organosilicone, surface tension.

MISTURA EM TANQUE DE CLORANTRANILIPROLE E FERTILIZANTES FOLIARES À BASE DE MANGANÊS: IMPACTO NAS CARACTERÍSTICAS REOLÓGICAS, PROPRIEDADES DE DEPÓSITO E PENETRAÇÃO CUTICULAR

RESUMO

O entendimento preciso das interações dos adjuvantes, agroquímicos e fertilizantes foliares é essencial para melhorar a eficácia das pulverizações. Neste estudo, exploramos a influência de fertilizantes foliares de manganês (sulfato de manganês e nitrato de manganês) misturados a um inseticida (clorantraniliprole) e um surfactante organosiliconado nas propriedades reológicas da solução, penetração cuticular e características de depósito em cutículas isoladas de tomate. Concentrações mais elevadas de $Mn(NO_3)_2$ induziram maiores ângulos de contato e tensões superficiais, enquanto maiores concentrações de $MnSO_4$ induziram apenas maior tensão superficial. A penetração cuticular (%) de $MnSO_4$ e $Mn\ (NO_3)_2$ foram, respectivamente, 3% e 21% da quantidade aplicada de Mn. A adição do adjuvante organosiliconado aumentou significativamente a penetração cuticular de ambos os sais para 20% para o $MnSO_4$ e 35% para o $Mn\ (NO_3)_2$. Ambos os sais de manganês, quando misturados em igual proporção, apresentaram uma penetração de 25%, o que não foi estatisticamente diferente de quando o adjuvante foi adicionado (23%). Os fertilizantes foliares não influenciaram a penetração cuticular do ativo clorantraniliprole. Nossos resultados confirmam o fato de que muitos processos não podem ser previstos para aplicações em campo. Assim, esses sistemas modelo podem ser usados para tentar entender e, em algumas situações, tentar prever o que poderia acontecer e entender seu comportamento e suas relações causais.

Palavras-chave: cutícula, fertilizantes, misturas, organosilicone, tensão superficial.

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 physical-chemical 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 physical-chemical properties, e.g. on the surface tension (Burkhardt et al., 2012; Zeng et al., 2015). Alterations of the physical-chemical properties of the spray solution might also induce changes in the droplet deposition pattern on leaf surface (Basi et al., 2012), and influence 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 physical-chemical 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, 2M, 3M and 4M; concentration series for Manganese nitrate (MN) was: 1M, 5M, 10M, 15M and 20M.

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.

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

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; Kraemaer 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 x 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 L^{-1} and percent (%) of the applied Mn.

For the micromorphological characterization of the deposit residues, dry deposits of the solutions on stomata-free cuticles from tomato fruits as well as on fresh hydrophobic barley leaf surfaces were generated with an environmental scanning electron microscope (ESEM, XL, FEI-Philips, Eindhoven, The Netherlands).

2.4 Third experiment – Impact of products mixture on cuticular penetration of Chlorantraniliprole and Mn

Treatment solutions were prepared with previous manganese salts [$MnSO_4$ and $Mn(NO_3)_2$], the adjuvant (BTS240) and one insecticide (chlorantraniliprole, MW 483.15 g mol^{-1}, water solubility 1.023 mg L^{-1} United States Environmental Protection Agency, 2008) on commercial formulation (Coragen®, 200 g L^{-1} a.i., Dupont, Delaware, USA). The treatments were described on Table 2:

Table 2. Chlorantraniliprole solutions influenced by manganeses salts and one organosilicone tank-mix adjuvants.

*Treatments	Salt Concentration (M)	Adjuvant Concentration (%)
Chlorantraniliprole (Chlt)	-	-
Chlorantraniliprole + $MnSO_4$	0.05	-
Chlorantraniliprole + $Mn(NO_3)_2$	0.05	-
Chlorantraniliprole + BTS240	-	0.05
Chlorantraniliprole + $MnSO_4$ + BTS240	0.05	0.05
Chlorantraniliprole + $Mn(NO_3)_2$ + BTS240	0.05	0.05
Chlorantraniliprole + $MnSO_4$ + $Mn(NO_3)_2$+ BTS240	0.025 + 0.025	0.05

*Chlorantraniliprole: 60g a.i. ha^{-1} Dose (commercial product) 100mL ha^{-1}; carrier volume 200 L ha^{-1}; corresponding to 0.05% v/v.

Surface tension and contact angle were determined as described above, the same for the determination of the cuticular penetration. Quantification of Mn was done with AAS as indicated above, while chlorantraniliprole was quantified according to the method described previously (Melo et al., 2015). The quantification of chlorantraniliprole was performed with High Performance Liquid Chromatography (Model Agilent 1260 Infinity LC) equipped with DAD detector at 254 nm (wavelength) and Vertex reversed-phase C18 column (250 mm x 4.0 mm, 5 µm), protected with a guard column (4 mm x 2.0 mm, RP-18, 5 μm, Phenomenex, Germany). HPLC grade acetonitrile:water (60:40, v/v) was used as mobile phase at 0.4 mL min^{-1} and 10 μL of injection volume. Under these operating conditions, the retention time of chlorantraniliprole was found to be 12.39 min. Identification of chlorantraniliprole was confirmed by comparing the retention time with authentic standard (chlorantraniliprole, Pestanal®, analytical standard - Sigma Aldrich, purity ≥ 98.0 %). A standard stock solution (300 μg mL^{-1}) was prepared in HPLC grade acetonitrile. All the standard solutions were prepared following QuEChERS method for the determination of chlorantraniliprole residues (Singh et al., 2012; Wilkowska and Biziuk, 2011) whereas standard solutions for cuticular penetration experiments were prepared directly by serial dilutions and stored at -4 °C before use. For quantitative analysis, calibration curves were obtained by injection of known concentrations.

2.5 Statistical analyses

Data from ST and CA were obtained by 10 replicates (droplets). For cuticle penetration a completely randomized design with 8 replicates for each treatment were done. All data were tested for normal error distribution using a Shapiro-Wilk normality test, for variance homogeneity by Levene's test, and for block additivity by the F-test of Tukey, at a 0.01 significance level, using SPSS Statistical Software, version 17.0 (SPSS Inc., Chicago, IL, USA). Values were compared by analysis of variance (Anova, $p \leq 0.05$); when applicable, means (± SE) were separated by Tukey multiple range test ($p \leq 0.05$).

3 RESULTS

3.1 First Experiment - Rheological properties of Mn salt solutions: impact of salt concentration

Surface tension of the solutions increased by raising salt concentrations and ranged between ~90 and 98 mN m^{-1} for $MnSO_4$ and ~80 and 110 mN m^{-1} for $Mn(NO_3)_2$ (Table 3, 4). The surface tension of water (72.1 mN m^{-1}) corresponded to the values presented in the literature.

In parallel to that, the contact angle on the hydrophobic tomato fruit cuticle decreased from 105 to 99 degrees with raising concentration of $MnSO_4$ (Tab. 1). For $Mn(NO_3)_2$ the contact angle increased at higher salt concentrations (Tab. 2), from 85° at

1M to 107° at 20M $Mn(NO_3)_2$. The surface tension values of $MnSO_4$ solutions were positively correlated with the concentration of the salt (Table 3). Distilled water showed the expected contact angle ranging between 99° - 101° on the tomato fruit cuticle.

Table 3.Surface Tension (mN m^{-1}) of $MnSO_4$ solutions and Contact Angle [°] of sessile droplets, determined on tomato fruit cuticles.

Treatments	**Surface Tension (mN m^{-1})**	**Contac Angle [°]**
$MnSO_4$ -1M	90.09 B	105.1 A
$MnSO_4$ -2M	93.36 C	103.0 AB
$MnSO_4$ -3M	95.45 D	99.7 AB
$MnSO_4$ -4M	98.22 E	99.2 B
Water	72.10 A	101.6 AB
CV (%)	0.27	5.03
F	18120.313*	3.413*

Different uppercase letters in the same column indicate differences according to the Tukey's test at 5% significance level. F – ANOVA Probability value of each treatment * significant at 5%. Density values: Water density – 0.9970; $MnSO_4$ - 1M – 1.3586; $MnSO_4$ - 2M – 1.5019; $MnSO_4$ – 3 M – 1.6096; $MnSO_4$ – 4 M – 1.7239;

Table 4. Surface Tension (mN m^{-1}) of $Mn(NO_3)_2$ solutions and Contact Angle [°] of sessile droplets, determined on tomato fruit cuticles.

Treatments	**Surface Tension (mN m^{-1})**	**Contac Angle [°]**
$Mn(NO_3)_2$ -1M	78.41 B	84.9 C
$Mn(NO_3)_2$ -5M	82.27 C	103.2 AB
$Mn(NO_3)_2$ -10M	102.69 D	102.6 AB
$Mn(NO_3)_2$ -15M	105.84 E	105.6 A
$Mn(NO_3)_2$ -20M	108.39 F	107.6 A
Water	72.10 A	99.1 B
CV (%)	0.34	4.57
F	26277.256*	35.549*

Different uppercase letters in the same column indicate differences according to the Tukey's test at 5% significance level. F – ANOVA Probability value of each treatment * significant at 5%.Density values: $Mn(NO_3)_2$ – 1 M – 1.1789; $Mn(NO_3)_2$ – 5 M – 1.4236; $Mn(NO_3)_2$ – 10 M – 1.7895; $Mn(NO_3)_2$ – 15 M – 1.8048; $Mn(NO_3)_2$ – 20 M – 1.9371.

3.2 Second Experiment - Rheological properties and cuticular penetration of Mn: impact of an organosilicone surfactant

3.2.1 Rheological properties of Mn salts and impact of BTS240

For this experiment we selected the 0.05 M salt concentration, which is commonly used for field applications. At this concentration, no significant impact of $MnSO_4$ and $Mn(NO_3)_2$ on surface tension and contact angle (Table 5) was observed. The surfactant alone caused a surface tension of 32 mN m^{-1} (0.05%) and 24 mN m^{-1} (0.5%), the contact angle decreased accordingly. When mixed in equal proportion without the adjuvant, the effect was still concentration-dependent but less pronounced, and also dependent on the type of the salt. In general, lower values were reached with the Mn nitrate salt at both adjuvant concentrations. In the mixture of both nitrate (50%) and sulfate (50%) salts with the adjuvant, an unexpected result was observed: at 0.05% adjuvant both ST and CA were similar as the adjuvant + $Mn(NO_3)_2$, but at the adjuvant concentration of 0.5% the ST drastically decreased, reaching lower values as the water + adjuvant alone (Table 5).

Table 5. Surface Tension (mN m^{-1}) of Manganse solutions and Contact Angle [°] of sessile droplets, with and without an organosilicone adjuvant in two concentrations, determined on tomato fruit cuticles.

Treatments	**Surface Tension (mN m^{-1})**	**Contac Angle [°]**
$MnSO_4$– 0.05M	72.96 A	93.2 A
$Mn(NO_3)_2$ – 0.05M	73.03 A	95.5 A
Mix – 0.05M	72.78 A	100.9 A
BTS240-0.05	32.23 F	65.9 B
BTS240-0.05 + $MnSO_4$	51.94 B	90.9 A
BTS240-0.05 + $Mn(NO_3)_2$	43.21 CD	95.1 A
BTS240-0.05 + Mix	42.92 D	91.2 A
BTS240-0.5	23.82 G	17.2 C
BTS240-0.5 + $MnSO_4$	44.86 C	76.8 B
BTS240-0.5 + $Mn(NO_3)_2$	37.44 E	96.3 A
BTS240-0.5 + Mix	18.82 H	76.5 B
CV (%)	2.75	10.67
F	2223.160*	75.069*

Different uppercase letters in the same column indicate differences according to the Tukey's test at 5% significance level. F – ANOVA probability value of each treatment * significant at 5%.

3.2.2 Cuticular Penetration of Mn

The cuticular penetration (%) of $MnSO_4$ and $Mn(NO_3)_2$ was 3% and 21% of the applied Mn amount, respectively. The 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 significantly different from 23% when the adjuvant was added (Fig 1).

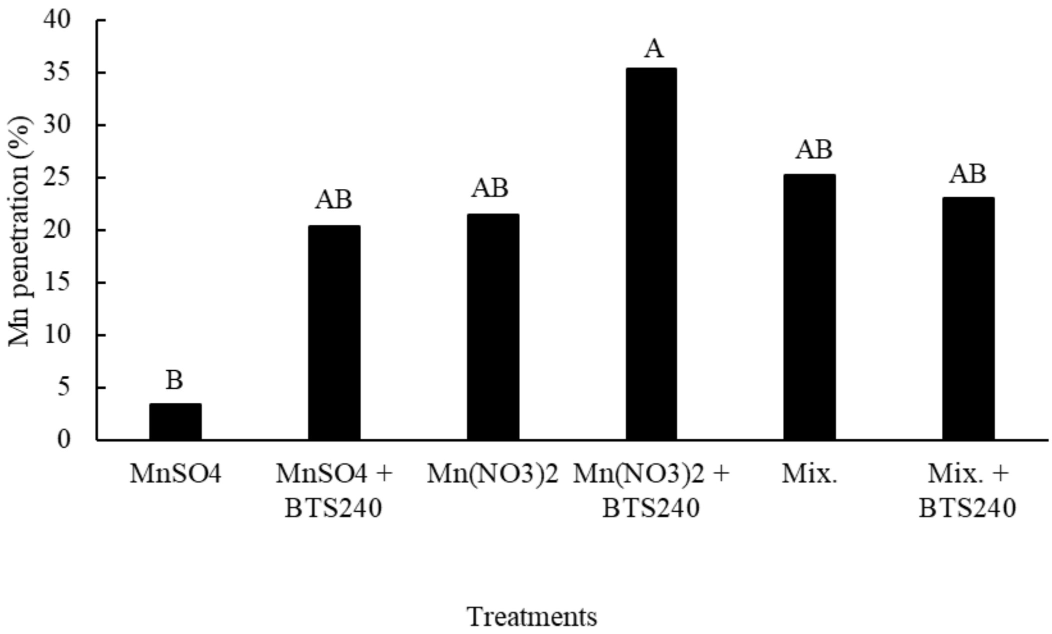

Fig 1. Cuticular penetration (%) of Mn from manganese salt solutions ($MnSO_4$, $Mn(NO_3)_2$ and their mixture),with and without an organosilicone adjuvant, through astomatous tomato fruit cuticles. Mean ± SE (n = 8) followed by the same letter do not differ according to Tukey $p \leq 0.05$.

3.2.3 Deposit properties

On isolated tomato fruit cuticles, both $MnSO_4$ and $Mn(NO_3)_2$ formed a comparable droplet size as recorded by the droplet footprint on the cuticle. The salt residues, however, were heterogeneously distributed within the droplet footprint, mostly as congruent crusts of variable thickness (Fig. 2 arrows), and sometimes even as evident crystalline structures (Figs.2 A, C, E). The organosilicone adjuvant had two effects: first, the droplet spread over the surface causing a bigger droplet footprint, as viewed with the lower magnification (35x) in the ESEM micrographs (Figs. 2 B, D, F). The second effect was the absence of any salt deposits, presumably because the ions were evenly distributed within the whole droplet spread area.

On barley leaves, the Mn salts alone, mixed and in combination with the adjuvant had a very distinct deposit pattern (Fig. 3). The droplet footprint themselves were not as visible as on the tomato fruit cuticle. Moreover, the salt deposits were more or less spread over the entire surface. In specific cases, salts accumulated close to the stomata (Fig 3. A –arrows and B) and even grew in direction of the stomata (Fig 3. F, arrows).

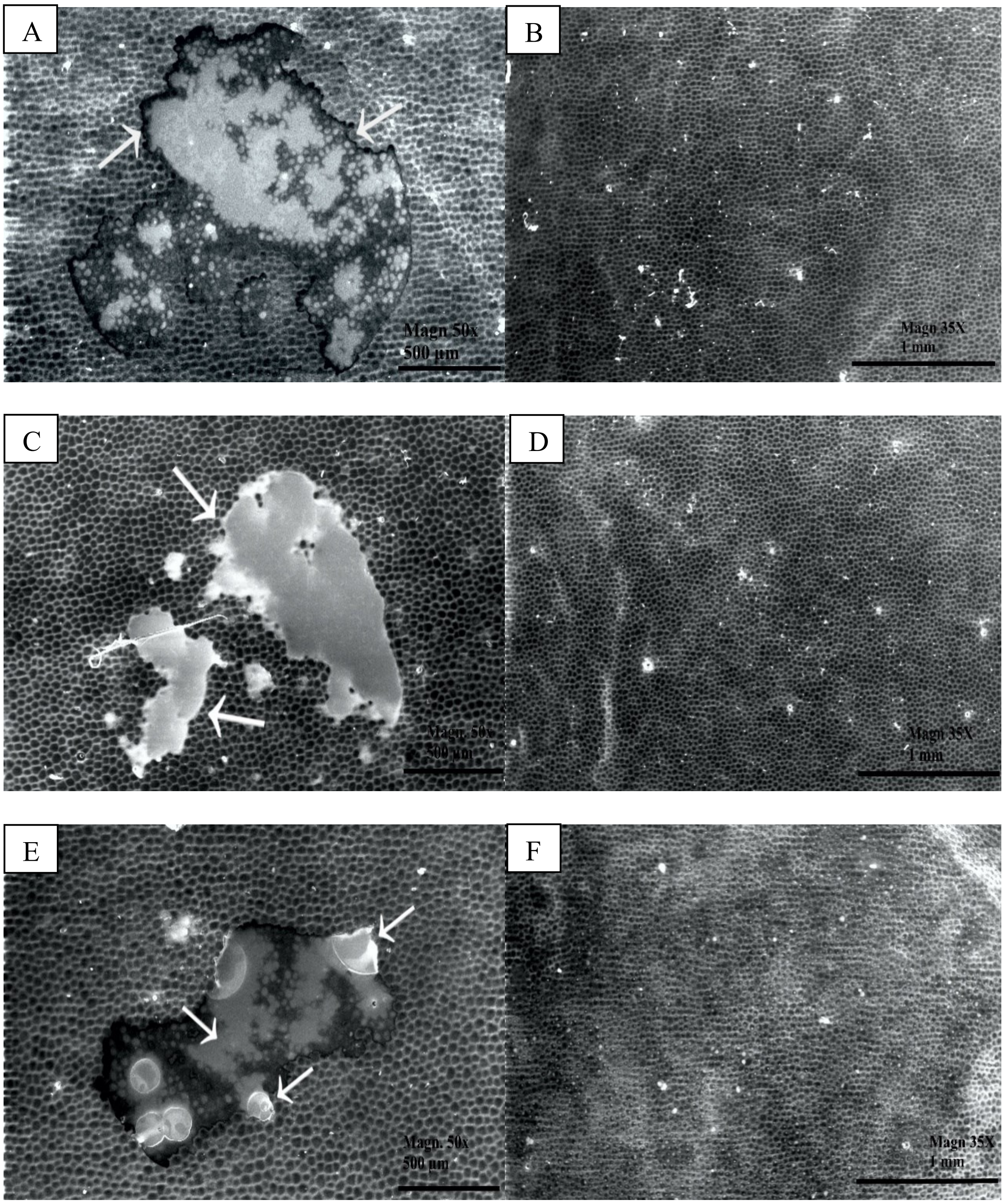

Fig 2. Representative micrographs of manganese salts on isolated tomato fruit cuticles. The pictures comprise the Manganese Nitrate 0.05M (A); BTS240 0.05% + Mn- Nitrate 0.05M (B); Mn Sulfate 0.05M (C), BTS240 0.05% + Mn Sulfate 0,05M (D) and their Mixture (E) and BTS240 0.05% + Mixture (F). Scale bar is given for each single figure.

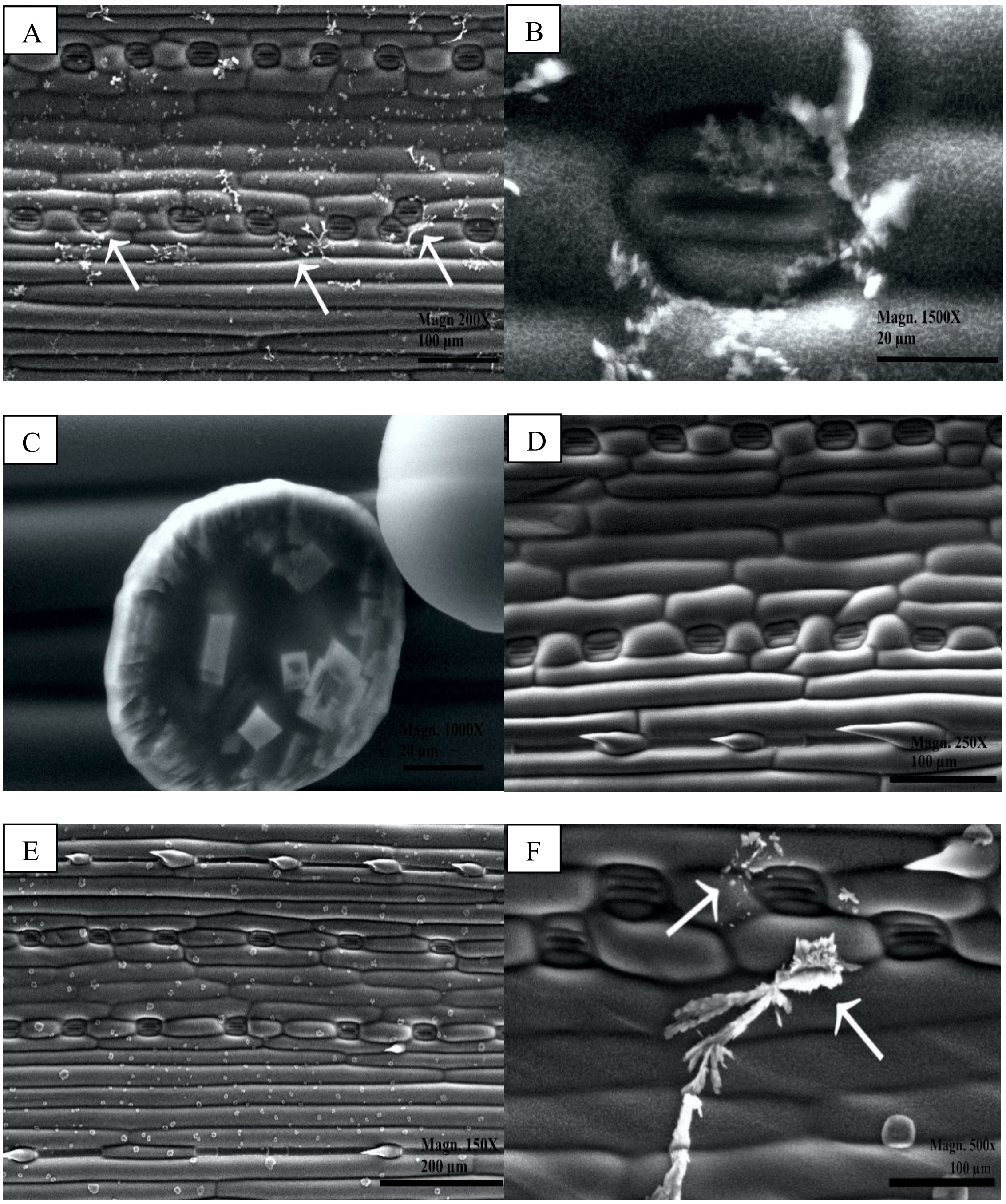

Fig 3. Representative micrographs of manganese salts on the hydrophobic, adaxial surface of barley leaves. The pictures comprise the $MnSO_4$ (0.05M) +BTS240 0.05% (A, B); $Mn(NO_3)_2$ (0.05M) +BTS240 0.05% (C, D); $MnSO_4$ + $Mn(NO_3)_2$ (0.05M) +BTS240 0.05% (E, F). Scale bar is given for each single figure.

3.3 Third Experiment - Impact of products mixture on cuticular penetration of Chlorantraniliprole and Mn

3.3.1 Rheological properties of all products mixture

Surface Tension (70 mN m^{-1}) and Contact Angle (90 degrees) of chlorantraniliprole solution remained unaffected by the addition of the manganese salts (Table 6). In combination with the adjuvant, ST decreased to values between 36 and 32 mN $m^{-1}$and the CA decreased to a value range between 54 and 41 degrees. The mixture of Chlorantraniliprole + both salts + adjuvants presented the lower ST results, while the contact angle did not differ statistically between all the solutions containing the organosilicone adjuvant and the manganese salts.

Table 6. Surface Tension (mN m^{-1}) and Contact Angle [°] of Chlorantraniliprole solutions through tomato fruit cuticles as influenced by manganese salts and one organosilicone tank-mix adjuvants.

Treatments	Surface Tension (mN m^{-1})	CA (°)
Chlorantraniliprole	69.63 A	90.50 A
Chlorantraniliprole + $MnSO_4$	69.27 A	92.33 A
Chlorantraniliprole + $Mn(NO_3)_2$	69.03 A	88.77 A
Chlorantraniliprole + BTS240 0.05%	36.18 B	41.74 C
Chlorantraniliprole + $MnSO_4$ + BTS240 0.05%	34.52 C	52.27 B
Chlorantraniliprole + $Mn(NO_3)_2$ + BTS240 0.05%	34.02 C	52.43 B
Chlorantraniliprole + $MnSO_4$ + $Mn(NO_3)_2$+ BTS240 0.05%	32.40 D	54.13 B
CV (%)	1.25	11.42
F	9300.397*	81.363*

Different uppercase letters in the same column indicate differences according to the Tukey's test at 5% significance level. F – ANOVA probability value of each treatment * significant at 5%.

3.3.2 Cuticular penetration of Mn and chlorantraniliprole

The cuticular penetration of manganese from $MnSO_4$ + chlorantraniliprole (47%) and $Mn(NO_3)_2$ + chlorantraniliprole (37%) strongly decreased with the addition of the surfactant, reaching values of 14% and 8%, respectively. In the solution containing both salts in equal proportion, as well as the insecticide and the adjuvant, cuticular penetration was of 38% of the applied manganese (Fig 4).

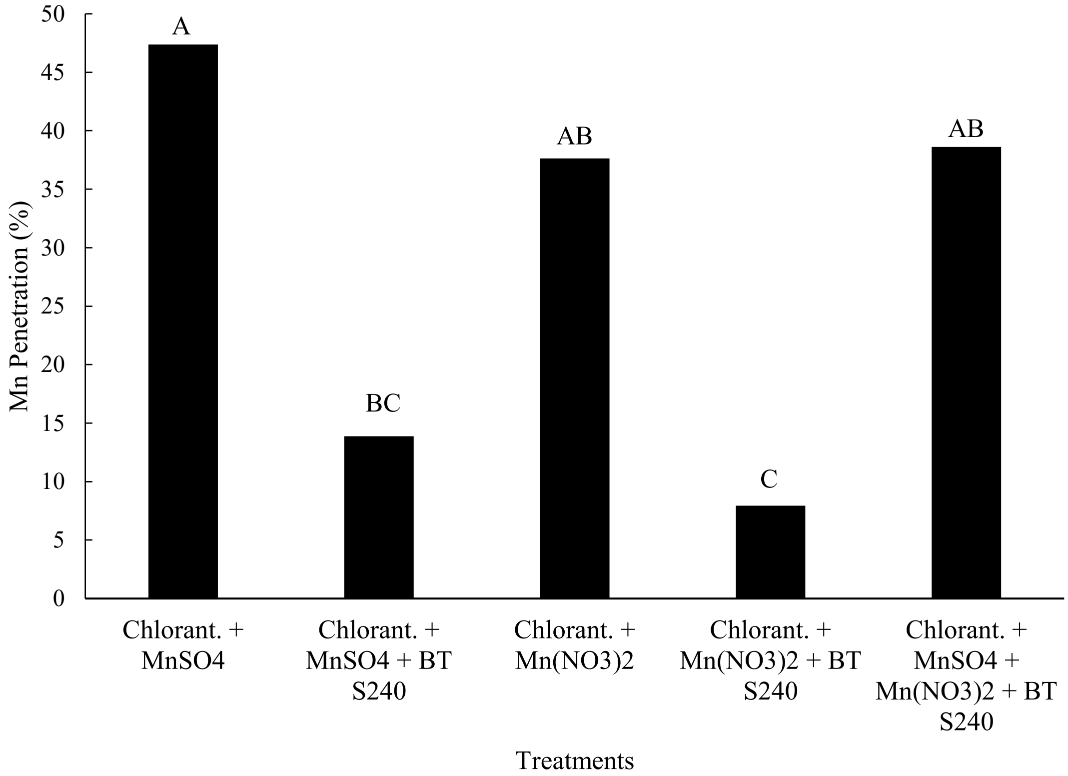

Fig 4. Cuticular penetration (%) of Mn from manganese salt ($MnSO_4$, $Mn(NO_3)_2$) and their mixture solutions, with or without an organosilicone adjuvant, through astomatous tomato fruit cuticles. Means followed by the same letter do not differ according to Tukey $p \leq 0.05$.

With an additional experiment, we evaluated the penetration of chlorantraniliprole as influenced by the other compounds. Statistically, there was no significant difference between the experimental groups concerning the penetration of chlorantraniliprole. As shown (Fig 5), insecticide alone had a very low penetration (3%) which increased to 4%, 10% and 12% with the addition of $MnSO_4$, $Mn(NO_3)_2$ and the organosilicone surfactant, respectively. In the combination of insecticide + Mn salt + adjuvant, penetration was at 10% level, irrespective of the Mn salt. However, the combination of both salts + insecticide + adjuvant kept the cuticular penetration (4%) at a similar level as the insecticide without any additive.

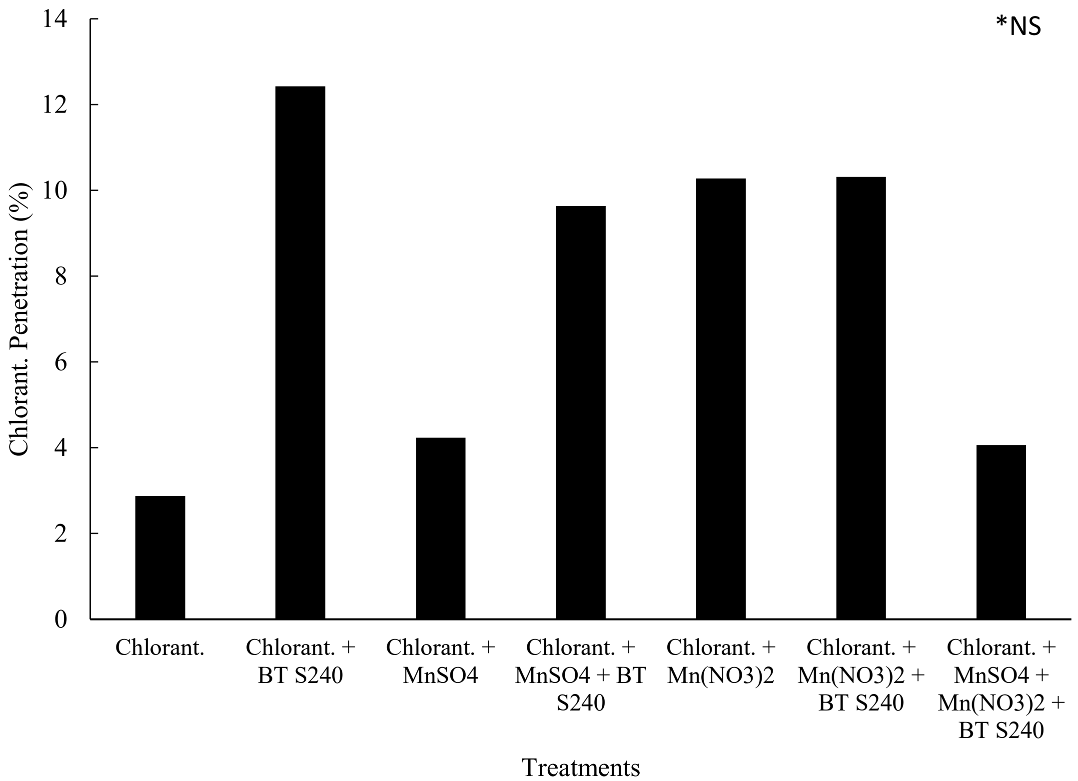

Fig 5. Cuticular penetration (%) of chlorantraniliprole through astomatous tomato leaf cuticles as influenced by manganese salts and one organosilicone adjuvant. *NS – indicates no significant differences according to the analyses of variance $p \leq 0.05$.

4 DISCUSSION

Aiming to get a better insight into the complex interaction between foliar fertilizers, agrochemicals and tank-mix adjuvants, we studied the impact of the products alone or in combination on the rheological properties of the solutions and the consequences for cuticular penetration. With a concentration gradient of the manganese salts above 1 M, ST and CA values changed significantly. However, at the salt concentration similar to that used in real foliar fertilization (0.05M), there was no significant cross-interaction between ions and insecticide, while the decrease of the ST by the organosilicone surfactant was very evident.

In general, when both adjuvant and salts were in the solution, cuticular penetration was related to surface tension, except when both Mn salts were at the same time in the mixture (Table 4). Alexander and Hunsche (2016) evaluating the cuticular penetration of different salts, found about 22% of penetration for manganese sulfate (without the use of adjuvant) through tomato fruit cuticles. In the current study we observed penetration values ranging from 4 to 20% for $MnSO_4$ and 20% to 35% for $Mn(NO_3)_2$. Overall, the efficacy of nutrient solution uptake by leaves depend of the physical-chemical properties of the spray solution such as solubility, electric charge, pH, surface tension or point of deliquescence (Fernández and Eichert, 2009; Fernández and Brown, 2013).

The fate of agricultural sprays on leaf surfaces during water evaporation and consequent droplet dry-down process is unclear. Complex mixtures of inorganic and organic compounds lead to physical-chemical properties that are governed by mutual interactions between the compounds in an increasingly concentrated state. Different from the general perception, this aqueous state of water soluble compounds (mostly salts) near to saturation may persist even during daytime and under sunny, dry ambient conditions (Burkhardt and Hunsche, 2013). This behavior is expected in first order for the inorganic salt compounds and is due to i) the hygroscopic nature of the compounds, ii) the undisturbed leaf boundary with elevated humidity, and iii) the stomatal transpiration as the main source of water vapor, and comparable to physical-chemical situations as in activated aerosols, i.e., atmospheric cloud condensation nuclei.

We did not see the ion specific effects on surface tension and contact angles that we would have expected when measuring highly concentrated salt solutions of the two manganese salts. Following the Hofmeister series, the sulfate anion, considered as kosmotropic (or structure maker), was expected to increase the surface tension while the chaotropic (or structure breaker), nitrate, should reduce it (Leroy et al., 2010). A strong decrease of the surface tension of $MnCl_2$ had been observed previously (Zeng et al, 2015). The concept of structure makers and structure breakers was not confirmed in pure salt solutions in another study, where the salts enhanced the surface activity of surfactants (Ozdemir et al., 2009). It cannot be excluded here that dynamic effects on a microscopic level could (e.g., humidity fluctuations) still lead to local reductions of surface tension and could enhance have enhanced the cuticular penetration of $Mn(NO_3)_2$ in comparison with $MnSO_4$.

Ions reduced surfactant activity, and this reduction was more noticeable for CA than for ST. For 0.05 % BTS240, a CA decrease was observed for the ion free solution, but not with any of the salts. For 0.5% BTS240, there was a CA decrease for sulfate solution and the mix, but not for the nitrate solution (Table 5). Nonionic as well as ionic surfactants are affected by pH and ions that can affect micellization, micellar growth, and critical micelle concentration (CMC) (Knoche et al., 1991). Chaotropic ions like nitrate increase the viscosity of surfactants more strongly than cosmotropic ions (sulfate) (Abezgauz et al., 2010). Sulfate might have counteracted the effect of nitrate, as kosmotropic and chaotropic substances can mutually neutralize (Alves et al., 2015). These reduction effects on surfactant activity were partly also seen for surface tension (ST), but the effect on CA might have been stronger due to additional influences from the surface.

The penetration experiments happened at RH 90%. Under these conditions, both sulfate and nitrate solutions did not fully evaporate, but reached high concentrations. However, $MnSO_4$ which has a deliquescence humidity (DRH) of 86% (Robinson and Stokes, 1970) was closer to saturation than $Mn(NO_3)_2$ which has a DRH of 3% (Gmelin, 1975; Berresheim and Jaeschke, 1986) and thus had a large amount of water absorbed, reducing the concentration gradient. In both cases, the addition of BTS240 surfactant reduced penetration (Fig. 1). According to the SEM images (Fig. 2 B, D, F), the solutions with the surfactant were more evenly distributed on the cuticular surface which could possibly have reduced local gradients and thus penetration.

The deposit structure of the treatments on isolated tomato fruit cuticles and barley leaves was markedly different between treatments, in particular when the surfactant was used (Fig 2, 3). This is not unexpected since deposit size and pattern strongly depends on the surface morphology (Alexander and Hunsche, 2016), as well as the dynamic changes happening in the underlying substrate. While the model system using isolated tomato fruit cuticle is a dead and dry tissue and changes might be limited to the absorption of water from the applied droplets, barley leaves are constituted by living cells showing metabolic and physiological processes. In particular, the gas and water exchange of the leaves in the time between droplet application and ESEM analysis might influence properties of the deposit residues (Fig 3.). Besides the differences observed in the deposit microstructure, the adoption of a valid model system - as done here with isolated tomato fruit cuticles - allows comparisons of the treatment solutions under standardized conditions.

In a previous study, Basi et al. (2014) highlighted the effects solutions containing different ions (Hofmeister series) on the absorption of compounds via stomata, activating the mass flow and enabling higher stomatal penetration of herbicides. With the hydraulic activation of stomata (HAS), the hygroscopic crystalline particles rise the contact area with the surface, promoting the spatial expansion of the salt crystals, forming thin layer on the walls of the stomata, providing the connection between the leaf surface and the apoplast, and increasing the penetration of liquid through the stomata (Burkhardt et al., 2012). However, the exact role of the Hofmeister classification on the cuticular penetration requires additional detailed studies.

The cuticular penetration of chlorantraniliprole through isolated tomato fruit cuticles showed penetration values around 7.5%, with no significant differences among treatment groups. This result confirms the low capability of chlorantraniliprole to permeate across hydrophobic leaf cuticles (Melo et al., 2015). Chlorantraniliprole is primarily active on chewing pests by ingestion and by contact (Bassi et al., 2009), and the physical properties of it confer xylem mobility with upward plant translocation, especially when applied to the root zone in soil applications or with seed treatments. Phloem mobility with foliar applications was not commonly observed (Selby et al 2017). However, it remains open if the Mn salts and the adjuvant used in this study improve the movement of the active ingredient in the plant, or if they affect the overall performance of the insecticide.

In theory, the presence of surfactant in the mixture could enhance the pesticide uptake by ensuring an intimate contact between the droplets and the leaf surface, especially on waxy species, directly related to the reduction of surface tension of the spray mixture. However, in many cases adjuvants might induce formation of a more amorphous deposit as compared to the product alone (Wang and Liu, 2007), with potential to influence penetration negatively.

In conclusion, the tank mixture of agrochemicals with foliar fertilizers and adjuvants is a very complex topic while the outcome is in most cases unpredictable under practical conditions. Nevertheless, scientific studies under standardized conditions might at least provide a better understanding of the potential effects of such mixtures. Our results confirm the fact that many processes cannot be predicted for field applications. Optimizations can be done for single components / formulations / systems, but the behavior under real conditions will never be under full control. There are simply too many variables: number, composition, and formulation of different products, compatibility of the products, quality of the water (pH, ions and temperature), application system and environmental conditions, and finally the target plant surface.

Thus, we can use this model systems to try to understand and in a few situations try to predict what could happen, and understand the behavior and causal relations only.

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CONFLICT OF INTERESTS

MH is Associate Professor at the University of Bonn and Head of the Research and Development unit of the company COMPO EXPERT GmbH and declares no conflict of interests.

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CHAPTER III - TANK MIXTURE OF INSECTICIDE, FOLIAR FERTILIZER AND ADJUVANT FOR *Tuta absoluta* AND *Neoleucinodes elegantalis* CONTROL IN TOMATO CROP

Tank mixture of insecticide, foliar fertilizer and adjuvant for *Tuta absoluta* and *Neoleucinodes elegantalis* control in tomato crop

ABSTRACT

The use of pesticides in tank mixture is important to reduce application costs and increase pest control mainly. The objective of this study was to evaluate the influence of manganese foliar fertilizers on the effectiveness of the insecticide chlorantraniliprole (Chlt) to control tomato leaf miner and tomato fruit borer in tomato crop under greenhouse conditions and to evaluate the possible effects of these mixtures on plant physiology. The experiment was conducted in a greenhouse, on randomized block design with eight treatments and four replications each. The treatments were: 1 – Chlt; 2 – Chlt + MnSO4; 3 – Chlt + Mn(NO3)2; 4- Chlt + Break-Thru (BTH); 5 - Chlt + MnSO4 + BTH; 6 – Chlt + Mn(NO3)2 + BTH; 7 – Chlt + MnSO4 + Mn(NO3)2 + BTH; 8 - Control. The physical chemical properties, physiological effects, pesticide efficacy and yield were evaluated. The results showed that the use of chlorantraniliprole in mixture with adjuvant and foliar fertilizers did not influence its efficacy against *Tuta absoluta* and *Neoleucinodes elegantalis*. Also, the mixture did not influence the chlorophyll content and all the nutrients content were in appropriate levels. We conclude that the tank mixture with manganese foliar fertilizers do not have influence over the efficacy nor the physiological characteristics. The physical chemical evaluations changed according to each manganese salt add in the mixture.

Keywords: chlorantraniliprole; manganese salts; adjuvant; organosilicon; pesticide efficacy;

Mistura em tanque de inseticida, fertilizante foliar e adjuvante no controle de *Tuta absoluta* e *Neoleucinodes elegantalis* no tomateiro

RESUMO

O uso de produtos fitossanitários em mistura é importante para redução de custos de aplicaçao e aumentar o espectro de controle de pragas, principalmente. Os objetivos deste trabalho foram avaliar a influência dos fertilizantes foliares sobre a eficácia do inseticida clorantraniliprole para as principais pragas na cultura do tomate, bem como os possíveis efeitos sobre a fisiologia da planta. O experimento foi conduzido em delineamento de blocos casualizados com oito tratamentos e quatro repetições, sendo: 1 – Clorantraniliprole (Chlt); 2 - Chlt + $MnSO_4$; 3 – Chlt + $Mn(NO_3)_2$; 4- Chlt + Break-Thru (BTH); 5 - Chlt + $MnSO_4$ + BTH; 6 - Chlt + Mn $(NO_3)_2$ + BTH; 7 - Chlt + $MnSO_4$ + Mn $(NO_3)_2$ + BTH; 8 - Controle. Foram avaliados: propriedades físico-químicas da calda, parâmetros fisiológicos das plantas, eficácia de controle e produtividade. Os resultados mostraram que o clorantraniliprole em mistura com adjuvante e fertilizantes foliares não influenciaram sua eficácia contra *Tuta absoluta e Neoleucinodes elegantalis*. Além disso, a mistura não influenciou o teor de clorofila e todo o conteúdo foliar de nutrientes estava em níveis apropriados. Concluiu-se que a mistura em tanque com fertilizantes foliares de manganês não tem influência sobre a eficácia do inseticida, nem sobre as características fisiológicas avaliadas. As propriedades físico-químicas variam de acordo com cada sal de manganês adicionado na mistura.

Palavras-chave: chlorantraniliprole; sais de manganês; adjuvante; organosiliconado; eficácia inseticida;

1 INTRODUCTION

The tomato (*Solanum lycopersicum* L.) is one of the most grown vegetables in the world being economically and socially important. Brazil is among the top 10 tomato producers with 4.39 million metric ton, in a cultivated area of 64.80 thousand hectares (IBGE, 2017). Its fruits are an important source of dietary antioxidants such as lycopene, phenolic compounds and vitamins C and E (Dominguez et al., 2012).

Insect pests such as *Bemisia tabaci*, *Frankliniella schultzei*, *Tuta absoluta* and *Neoleucinodes elegantalis*, frequently attack the tomato plant, and intense infestation can happen throughout the whole crop cycle, since sowing until harvesting. Even in greenhouses, attacks can cause considerable damage (Alvarenga, 2004). The most important of them are the tomato leaf miner - *Tuta absoluta* – considered one of the main entomological problems of tomato, attacking leaves, branches and fruits (Villas Bôas et al., 2009). The tomato fruit borer - *Neoleucinodes elegantalis* is another pest that can cause reduction on tomato yield as well as unfit the fruit for consumption for both industry and *in natura* (Bezenga et al., 2010).

Due to this high number of pests reaching the crop, the use of pesticides is frequent and in some cases, they exceed three weekly applications, reaching more than 35 applications per crop cycle. This leads the growers to choose the tank mixture of pesticides, and this have become a common practice in Brazilians fields, in order to keep the crop productivity. The main problem is the uncertain effects that each mixture of different products can cause on the application (Gazziero et al., 2015).

Besides this, the combination of a xenobiotic (insecticide, fungicide, and herbicide) with an adjuvant and a foliar fertilizer is one of the most common mixtures made on field. Mattos et al. (2002) emphasized the need to conduct studies related to the administration of pesticides together, considering that these products are rarely applied individually in the crops.

Some pesticides can affect plant physiology mainly in photosynthetic redox chain (Jones et al., 1986) as well as some adjuvants could increase the spray spread over the leaf surface, influence some physical-chemical characteristics (Cunha, Alves and Reis, 2010) and increase the uptake of some products (Mackinnon et al., 2009).

Associations between products may have advantages compared to the application of a single compound due to the increase in efficiency against the target organisms and the reduction of applied quantities and costs (Gazziero et al., 2015).

Given that, studies are needed to demonstrate whether such mixtures influence the efficacy of pest and disease control.

Castro (2009) has already highlighted the importance of determining concentrations of pesticide combinations that cause harmful effects on non-target species, as well as the need to carry out experimental studies related to the joint exposure of agrochemicals. Specifically, for tomato, joint actions of pesticides need clarification, including foliar fertilizers and possible influences on the physiology of this crop.

Therefore, the objective of this study was to evaluate the influence of manganese foliar fertilizers on the effectiveness of the insecticide chlorantraniliprole over *Tuta absoluta* and *Neoleucinodes elegantalis* in the tomato crop, as well as to evaluate the possible effects of these mixtures on plant physiology.

2 MATERIAL AND METHODS

2.1 Experimental Site

The experiment was conducted in a greenhouse, located at Gloria Farm (18° 57'S and 48° 12'W), belonging to the Federal University of Uberlândia. The plots were spaced 0.7 m between plants and 0.9 m between rows (3.15 m^2 each plot), totalizing 201.6 m^2 area with plant density of 15,800 plants ha^{-1}. Soil analyzes were performed at the experiment site and the results were presented in Table 1:

Table 1. Soil chemical attributes in greenhouse, Uberlândia, MG.

Layer	pH H_2O	P	K	Al	Ca	Mg	H+Al	SB	t	T	V	m	OM
m	(1:2.5)	mg dm^{-3}	-------------------- cmolc dm^{-3} ---------------								%		dag kg^{-1}
0-0.2	6.3	229.2	111	0.0	5.7	1.3	3.10	7.28	7.28	10.38	70	0	3.3
0.2-0.4	6.2	218.7	95	0.0	4.5	1.1	3.10	5.84	5.84	8.94	65	0	2.5

P, K = (HCl 0.05 mol L^{-1} + H_2SO_4 0.0125 mol L^{-1}) P available (extractor Mehlich-1); Ca, Mg, Al, (KCl 1 mol L^{-1}); H + Al = (Tampon solution - SMP at pH 7.5); SB = Sum of basis; t = cation-exchange capacity (CEC) effective; T = CEC in pH 7.0; V = Saturation for basis; m = Saturation for aluminum; OM = organic material (EMBRAPA, 2009).

2.2 Treatments

The treatment solutions were prepared with two manganese salts (Manganese sulfate and Manganese nitrate), one adjuvant (trisiloxane-based super spreader Break-Thru® S240) and one insecticide (chlorantraniliprole (Chlt), MW 483.15 g mol^{-1}, water solubility 1.023 mg L^{-1}, United States Environmental Protection Agency, 2008) on commercial formulation (Premio®, Dupont, Delaware, USA).

Solutions of Manganese Sulfate and Manganese Nitrate (0.05 M) were prepared with the adjuvant Break-Thru (BTH) (0.05 %, v/v) and the insecticide (60 g AI ha^{-1}; 100 mL ha^{-1}; spray volume 200 L ha^{-1}; corresponding to 0.05% v/v). The treatments were as follows: 1 – Chlt; 2 – Chlt + MnSO4; 3 – Chlt + Mn(NO3)2; 4- Chlt + Break-Thru (BTH); 5 - Chlt + MnSO4 + BTH; 6 – Chlt + Mn(NO3)2 + BTH; 7 – Chlt + MnSO4 + Mn(NO3)2 + BTH.

2.3 Experiment conduction

Tomato seeds of the hybrid 'Débora Max', 'Santa Cruz' group of undetermined growth, were sowed in polyethylene trays (200 cells) containing agricultural substrate until the development of 5 to 7 final leaves, when they were transplanted. On May 16th, 2017 (15 days after sowing) the transplant were carried out.

The planting fertilization consisted in the application of 318 g of the formula NPK (04-14-08) per plot. Cover fertilization was carried out during the recommended periods for full development of the crop, according to Alvarenga (2004).

Drip irrigation was used, with a nominal flow of 3.8 L h^{-1} m^{-1} at 70 kPa of service pressure and with emitters every 0.50 m. The crop was irrigated during the whole cycle, initially, with two 15-minute shifts per day, which passed to three shifts of 15 minutes in the beginning of flowering.

For diseases control, preventive applications with protective fungicides were applied, using mancozebe + azoxistrobin (Unizeb Gold + Amistar wg – 80g c.p. and 300 g c.p. per 100 L of water). Weed control was done manually.

It was adopted one rod per plant system. Crop dealings were carried out according to the need and development of the crop. The plants were stamped with individual bamboo stakes vertically, every 5 meters and use of iron wire (horizontally) and polyethylene wire (vertically). The polyethylene wire was tied at the base of the plant and suspended vertically, being fixed in a galvanized iron wire, stretched over the line of plants at 2 m high and attached at its ends to wooden stakes.

On August 3th (79 days after the transplanting – DAT), the treatments were applied, when the average number of leaves per pointers attacked was 4%. For the applications it was used a compressed CO_2 propellant sprayer equipped with a boom containing three Magnojet MGA04 hollow cone tips, with a working pressure of 40 Psi and a spray volume of 487 L ha^{-1}. The sprayer boom was used vertically, so that all parts of the plant received the same volume of spray. The mean climatic data at the time of application were: temperature 24.0 °C; relative humidity 37.5 %; wind speed 2.7 km h^{-1}.

2.4 Evaluations

2.4.1 Physical-chemical evaluations

Different tank mixtures were prepared to evaluate the physical-chemical characteristics: density, pH, electric conductivity (EC) and viscosity. In the ways of comparison, it was evaluated distilled water. The evaluations were done as described elsewhere (Cunha et al., 2009). The evaluations of physical-chemical properties were realized on the Agricultural Mechanization Laboratory (LAMEC), from the Federal University of Uberlândia, Campus Uberlândia.

2.4.2 Pest Evaluation

The main pests evaluated were Tomato pinworm or leaf miner (*Tuta absoluta*) and the Tomato fruit borer (*Neoleucinodes elegantalis*). For each type of pest, specific sampling methods were performed.

Evaluations of treatments efficacy for tomato leaf miner were carried out in addition to the previous count, at five, seven and 10 days after application (DAA), counting the number of leaf miner attack symptoms (mines) or verification of galleries in the fruits of the first cluster, found in five plants per plot. The control level adopted was 20% of leaves or 1% of fruits damaged (Silva & Carvalho, 2004).

The tomato fruit borer was evaluated from the fruiting, with 5 plants per plot being sampled, observing the number of fruits with caterpillars input signals. The control level adopted was 5% of fruits with freshly hatched caterpillars or 1% for fully developed caterpillars (Benvenga et al., 2010).

2.4.3 Physiological evaluations (Foliar chlorophyll index and chlorophyll a fluorescence)

The physiological evaluations were realized during the morning one day before the first treatment application and one day after the insecticide application.

The evaluation of chlorophyll index was made with a chlorophyll meter (model SPA-502 Konica-Minolta). In each leaf five leaflets were evaluated, being two from each side and one terminal leaflet, representing the whole leaf surface.

The same plants used in the determination of chlorophyll index were selected to measure the chlorophyll a fluorescence. The minimum (F0) and the higher (Fm) fluorescence of the chlorophyll a in the photosystem II (PSII), in adapted dark conditions, were evaluated with a fluorescence analyses of chlorophyll a (Mini-PAM, Walz). The adapted dark condition was established after 30 minutes of simulated dark with metal clips for leaves (DLC-8). In this condition, it was evaluated the PSII fluorescence after one pulse of light saturation (0.8 s) and calculating the PSII maximum quantum yield (ØPSII=[Fm-F0]/Fm).

2.4.4 Foliar nutrient content

Leaf samples were collected for nutrient content analysis at 64 DAT, removing a fourth leaf from the apex. For chemical analysis, the sampled material was washed with deionized water and dried in a forced air circulation oven at 70 °C for 72 hours. Then, the samples were crushed in a Wiley type mill, equipped with a 20 mesh sieve. N-total was determined by the Kjeldahl method. The elements P, K, Ca, Mg, S, Fe, Mn, Zn and Cu were analyzed after mineralization by nitric-perchloric digestion.

2.4.5 Tomato yield (t ha^{-1})

The harvest started when most fruits of the cluster presented a red coloration. It was made in two different times, the first on August 17th and the second on August 29th. The average yield (t ha^{-1}) of both harvests, was determined from the tomato production data per plant (fruits from all plants of the plot where collected), in which the average fruit yield was extrapolated to an area of 15,800 plants, equivalent to the number of plants found in one hectare, in the spacing used in the experiment.

2.5 Experimental design and statistical analysis

The experiment was conducted in randomized block design (RBD), with eight treatments (seven solutions and a control) and four replications. The obtained data was submitted to normality test of normal distribution of errors (Shapiro Wilk), homogeneity of variances from Levene and additivity block test by the Tukey F test, in 0.01 of significance.

The "F" test was performed to determine levels of significance of 0.05 and 0.01 for the analysis of variance. When these tests were significant, the averages were compared with the Scott-Knott test at 0.05 level of probability. When necessary data was transformed by square root (x+1).

3 RESULTS AND DISCUSSION

3.1 Physical-chemical evaluations

The results showed that the addition of manganese sulfate as well the manganese nitrate into the mixture, individually or together in the mixture, reduced the pH and EC (Table 2).

Table 2. Physical-chemical characteristics of water and pesticide mixtures used in tomato crop.

Treatments	Hydrogen potential (pH)	Electric conductivity (µS cm^{-1})	Viscosity (mPa s^{-1})
Chlorantraniliprole	6.16 C	5.57 B	0.95 B
Chlorantraniliprole + $MnSO_4$	5.91 E	4.92 C	1.01 A
Chlorantraniliprole + $Mn(NO_3)_2$	6.01 D	2.76 F	0.91 C
Chlorantraniliprole + BTH	6.68 A	6.07 A	1.00 A
Chlorantraniliprole + $MnSO_4$ + BTH	6.17 C	4.83 C	1.02 A
Chlorantraniliprole + $Mn(NO_3)_2$ + BTH	6.04 D	4.68 D	1.01 A
Chlorantraniliprole + $Mn(NO_3)_2$ + $MnSO_4$+ BTH	6.34 B	3.85 E	1.02 A
Water	5.02 F	1.18 G	1.01 A
CV(%)	1.02	1.79	1.20
F	179.407*	1329.253*	30.443*
F_{levene}	4.219^{ns}	3.835*	1.057*
SW	0.942*	0.929*	0.969*

Uppercase letters in same column indicate differences according to the Scott-Knott test at 0.05 level of significance. F- values of calculated F for different treatments.

The viscosity was more influenced by the nitrate salt, with a decrease in the value. The other mixtures values presented the same results than water. In comparison between the two fertilizers, the nitrate salt presented lower values of pH and EC than the sulfate (Table 2).

Each foliar fertilizer has a different effect over the physical-chemical characteristics when added to chlorantraniliprole. BTH is a wide used adjuvant and its use is very common in Brazilian fields. Research indicates that this adjuvant can reduce the spray pH as well as EC. As described by Cunha et al. (2010), viscosity did not change statistically from different treatments.

The incompatibility in tank mixtures can be minimized with the use of adjuvants and pH reducers. The active molecules ingredient, when in solution, dissociate into ions, which can be negative and positive charges, being able to bind to other ions present in the solution, possibly forming precipitates (Petter et al., 2012; Theisen & Ruedell, 2004), which did not occur in the present study. As higher was the acid dissociation constant (Ka) or lower is the basic dissociation constant (Kb), lower is the compound capacity to dissociate in aqueous solution and still have the capacity to form other molecules. This is a peculiar characteristic of each product, which may determine its behavior in mixture (Minguela and Cunha, 2010).

3.2 Pest Evaluation

The number of caterpillars had all decreased in comparison to the control for almost all the mixtures, except the one with chlorantraniliprole and the adjuvant. All mixtures had reduced the values of brocaded fruits comparing to the control (Table 3).

Table 3. Average number of *Tuta absoluta* caterpillars and brocaded fruits as function of the application of mixtures of phytosanitary products in the tomato crop.

Treatments	**Caterpillar^{A}**	**Brocaded Fruits^{A}**
Chlorantraniliprole	0.06 A	1.32 A
Chlorantraniliprole + $MnSO_4$	0.31 A	1.18 A
Chlorantraniliprole + $Mn(NO_3)_2$	0.19 A	1.48 A
Chlorantraniliprole + BTH	0.38 AB	1.43 A
Chlorantraniliprole + $MnSO_4$ + BTH	0.19 A	1.27 A
Chlorantraniliprole + $Mn(NO_3)_2$ + BTH	0.19 A	1.06 A
Chlorantraniliprole + $Mn(NO_3)_2$ + $MnSO_4$+ BTH	0.12 A	1.23 A
Control	0.81 B	2.06 B
CV(%)	57.02	70.46
DMS	0.397	0.556
F	5.709*	5.798*
F_{levene}	9.882^{ns}	11.040^{ns}
SW	0.852^{ns}	0.929^{ns}

Uppercase letters in same column indicate differences according to the Tukey test at 0.05 level of significance. F- Values of calculated F for different treatments. ^{ns};*;^{A} - not significant; significant at 0,05. Transformed data by square root (x+1.0)

After the treatments application, it was observed a significant reduction in the average number of caterpillars (Table 4).

Table 4. Average number of *Tuta absoluta* as function of evaluation dates.

Dates	**Caterpillars**
Pre-application	0.78 B
5 DAA	0.15 A
7 DAA	0.15 A
10 DAA	0.03 A
CV(%)	57.01
DMS	0.248
F	18.470*
F_{levene}	9.882^{ns}
SW	0.852^{ns}

Uppercase letters in same column indicate differences according to the Tukey test at a 0.05 level of significance. F- values of calculated F for different treatments. ^{ns};* - not significant; significant at 0,05.

As presented in some research the main tomato pest control is well done by chlorantraniliprole (Abbas et al., 2015; Guimarães et al., 2010). Although some cases of resistant insect to diamides were reported in tomato crops (Ribeiro et al., 2017; Roditakis et al., 2017). In this study, the use of chlorantraniliprole in mixture with foliar fertilizers and adjuvant did not influence its efficacy.

Different results were showed by Vukovic et al. (2009) when studying the effects of the mixture (cypermethrin, azoxystrobin, mancozeb) with a complex fertilizer, depending on components and water quality over the mortality of *Leptinotarsa decemlineata*. The effectiveness of the double combinations was significantly increased (to 89–98%) by adding a fertilizer or a wetting agent. Regarding to the insecticide application, a significant increase in effectiveness was achieved only with the mixture cypermethrin + azoxystrobin + fertilizer.

3.3 Physiological evaluations

The physiological parameters evaluated did not present statistical significance (Table 5).

Table 5. Efficiency of photosystem II and chlorophylls index evaluations in tomato cultivar treated with different pesticides in mixture.

Treatments	**∅PSII[A]**	**SPAD[B]**
Chlorantraniliprole	0.61	44.55
Chlorantraniliprole + $MnSO_4$	0.62	44.56
Chlorantraniliprole + $Mn(NO_3)_2$	0.53	44.99
Chlorantraniliprole + BTH	0.60	47.79
Chlorantraniliprole + $MnSO_4$ + BTH	0.49	48.05
Chlorantraniliprole + $Mn(NO_3)_2$ + BTH	0.50	45.11
Chlorantraniliprole + $Mn(NO_3)_2$ + $MnSO_4$+ BTH	0.55	46.02
Control (04/07)	0.51	47.49
Pre-application (02/07)	0.60	47.01
CV	25.40	4.90
F	0.470^{ns}	1.599^{ns}
$\mathbf{F_{levene}}$	2.323*	1.049*
SW	0.964*	0.974*

A: maximum quantum yield of photosystem II (ØPSII =(Fm-F0)/Fm); *B*: SPAD chlorophyll index. F- values of calculated F for different treatments. ^{ns}; * - not significant; significant at 0,05.

In addition, it was found that the bioactivity of pesticides differed between compounds. Salem (2016) found that some insecticides within one insecticide class (organophosphate, carbamate, and pyrethroid) could reduce photosynthesis while other insecticides in the same class did not.

Physiological parameters were good indicators of plant physiological activity. These parameters can be correlated to yield. In some cases, pesticides applications affect metabolic pathways and could report an increase or decrease over crop growth as well as an adverse effect on plant photosynthesis. In some cases, the adjuvant presence in the mixture may be responsible for the noted effect on plant physiology (Jones et al., 1986).

The chlorophyll index did not vary in this study. Salem (2016) analyzing the effect of different insecticides such malathion and thiamethoxan over the chlorophyll content of maize and tomatoes found that some of these products could reduce the it in 9 to 80% during the evaluation time. According to Araújo et al. (2018) and Ferreira et al. (2006), SPAD index between 48 to 62 in tomato plants showed that these plants present nutritional and physiological status within the expected for good development, similar to those found in this work.

According to Shakir et al. (2016) pesticides application above the recommended dose can adversely affect tomato growth. At higher doses, all the tested pesticides caused toxic effects on all the studied parameters of tomato. Since pesticide dealers usually suggest farmers to apply pesticides in doubled doses to the recommended dose, it can be harmful and affect tomato growth and yield.

3.4 Foliar nutrient content

Tank mixture applications had influenced the concentration of phosphorus (P), Sulfur (S), Manganese (Mn) and Cupper (Cu).

Phosphorus content decrease in plants that received applications of the mixture with manganese sulfate and manganese sulfate with BTH. These treatments presented the same values as the control. Concerning to sulfur, the mixtures with BTH presented lower content than the control (Table 6).

Manganese content were higher in almost all the treatments that had the foliar fertilizers, in comparison to control and the treatments with chlorantraniliprole and with chlorantraniliprole with BTH. An unexpected value was presented for the treatments that had mixture application of manganese nitrate and the adjuvant that presented the same content as the control. For cupper, the lower contents were observed in the control and in the mixture with manganese sulfate and BTH (Table 6).

Table 6. Tomato foliar nutrient content in function of different pesticide mixture application.

Treatments	N	P	K	Ca	Mg	S	Fe	Mn[A]	Cu	Zn
	----------------------------			(g Kg^{-1})	------------------------		-----------------	mg Kg^{-1}	---------------	
Chlorantraniliprole	35.37	6.35 A	35.50	30.85	5.62	4.00 A	4.18	1.10 B	0.20 A	0.41
Chlorantraniliprole + $MnSO_4$	37.40	5.77 B	33.00	28.70	4.95	4.15 A	3.91	7.88 A	0.19 A	0.38
Chlorantraniliprole + $Mn(NO_3)_2$	37.82	7.00 A	36.00	29.62	5.80	4.57 A	4.18	5.75 A	0.21 A	0.38
Chlorantraniliprole + BTH	37.30	6.87 A	34.50	26.60	4.77	3.47 B	4.62	1.76 B	0.21 A	0.34
Chlorantraniliprole + $MnSO_4$ + BTH	31.10	5.07 B	28.62	26.87	4.67	3.35 B	4.60	11.47 A	0.15 B	0.36
Chlorantraniliprole + $Mn(NO_3)_2$ + BTH	31.87	7.60 A	31.87	32.72	5.67	3.22 B	3.32	3.43 B	0.23 A	0.39
Chlorantraniliprole + $Mn(NO_3)_2$ + $MnSO_4$+ BTH	34.32	6.45 A	33.37	23.95	4.67	3.20 B	3.91	6.75 A	019 A	0.45
Control	34.85	4.77 B	33.12	26.67	4.35	3.90 A	3.64	1.20 B	0.15 B	0.28
CV (%)	10.52	18.74	11.68	18.91	16.23	16.54	17.92	27.25	13.81	17.62
F	1.879^{ns}	2.762*	1.423^{ns}	1.090^{ns}	1.808^{ns}	2.602*	1.662^{ns}	7.165*	4.566*	2.397^{ns}
F_{levene}	2.503*	3.707^{ns}	1.255*	1.868*	2.352*	0.865*	2.436*	2.649*	4.367^{ns}	2.274*
SW	0.988*	0.954*	0.970*	0.968*	0.982*	0.981*	0.933*	0.874^{ns}	0.949*	0.967*

Uppercase letters in same column indicate differences according to the Scott-Knott test at 0.05 level of significance. F- values of calculated F for different treatments. ^{ns};*;^{A} - not significant; significant at 0,05; transformed data by square root (x+0.5)

According to Malavolta and Vitti (1997), all the nutrients content was in appropriate levels. As sulfur present mobility in phloem, it is expected lower concentration in treatments that the element was not applied. However, on the treatment with manganese sulfate and BTH, the foliar concentration was lower than the treatment without BTH. Treatments with sulfate presented higher manganese concentration than the nitrate mixtures (Table 6). According to Mcfarlane and Berry (1974) monovalent ions have faster absorption through the cuticle than the divalent. Compounds like BTH, and organosilicone adjuvant can reduce the surface tension of the solution drastically and cause a spreading over the leaf surface (Alexander and Hunsche, 2016).

3.5 Tomato yield (t ha^{-1})

The average yield did not present statistical significance (Table 7). However, the total yield production was within the expected for the variety. It can be observed that although the insecticide treatments showed control effectiveness on the evaluated pests, they were not enough to influence tomato yield. Some research has also shown that the pest control effectiveness does not necessarily influence the tomato yield (Mattos et al. 2002; Liburd et al. 2000). However, Momol et al (2004) found an increase on tomato yield when virus transmitters (thrips) control was efficient.

Table 7. Tomato average yield (t ha^{-1}) in function of different pesticide mixture application.

Treatments	**Yield (t ha^{-1})**
Chlorantraniliprole	25.94
Chlorantraniliprole + $MnSO_4$	28.26
Chlorantraniliprole + $Mn(NO_3)_2$	38.08
Chlorantraniliprole + BTH	29.91
Chlorantraniliprole + $MnSO_4$ + BTH	30.01
Chlorantraniliprole + $Mn(NO_3)_2$ + BTH	29.90
Chlorantraniliprole + $Mn(NO_3)_2$ + $MnSO_4$+ BTH	40.04
Control	43.13
Average	33.16
CV(%)	57.60
F	0.964^{ns}
F_{levene}	3.040*
SW	0.933*

F- values of calculated F for different treatments. ^{ns};* - not significant; significant at 0,05.

Initially, it was expected at least two applications, but the control level was not achieved anymore after the first treatments application, in this case, it was made only one application and two harvest during the experiment period.

In addition, with the low presence of pests, there was a high concentration of white mold in the leaves. This fact caused a reduction of active leaf area and consequent fall, which may have influenced the physiological and agronomic evaluated parameters.

4 CONCLUSION

The physical-chemical evaluations changed according to each manganese salt added in the mixture. Chlorantraniliprole has efficacy over the *Tuta absoluta* and *Neoleucinodes elegantalis* and the tank mixture with manganese foliar fertilizers and organosilicon adjuvant did not have influence over the efficacy nor the physiological characteristics.

Nevertheless, more research over field conditions should be done, mainly with other fertilizes, to provide a better understanding on the tank mixture effects.

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CHAPTER IV - TANK MIXTURE OF PESTICIDES AND FOLIAR FERTILIZES FOR *Triozoida limbata* CONTROL IN GUAVA TREES (*Psidium guajava* L.)

Tank mixture of pesticides and foliar fertilizes for *Triozoida limbata* control in Guava trees (*Psidium guajava* L.)

ABSTRACT

Tank mixture of pesticides and foliar fertilizers is a common practice in agriculture but without a major scientific support. Thus, the objective of this study was to evaluate the effect of tank mixture of an organosilicon adjuvant and manganese foliar fertilizer on the imidacloprid insecticide effectiveness over *Triozoida limbata* control in guava trees. The experimental plot was considered with four trees followed in the same cultivation line subdivided into 4 quadrants. The experiment followed a randomized block design with split plots, with four replications. The treatments were T1 – Imidaclopride (Imid.); T2 – Imid. + Polyether-polymethyl siloxane copolymer (Sil.); T3 – Imid. + $MnSO_4$; T4 – Imid. + Sil. + $MnSO_4$; T5 – Control (no application). Physical-chemical characteristics, spray deposition over the leaves and losses to the soil; guava psyllid percentage of infestation and nymph's number were evaluated. The addition of foliar fertilizer on the mixture reduced the pH and surface tension and increased the electric conductivity and viscosity of the insecticide solutions. The silicon adjuvant reduced the surface tension and increased the viscosity and the pH. The tank mixture of organosilicon adjuvant and manganese foliar fertilizer do not influence the efficacy level of the insecticide.

Keywords: Guava psyllid; physical-chemical characteristics; neonicotin; foliar fertilizer; organosilicon.

Mistura em tanque de produtos fitossanitários e fertilizante foliar no controle de *Triozoida limbata* na cultura da goiabeira (*Psidium guajava* L.)

RESUMO

A mistura em tanque de produtos fitossanitários e fertilizantes foliares é uma prática comum na agricultura, mas ainda sem muito suporte científico. Assim, o objetivo deste trabalho foi avaliar o efeito da mistura em tanque de um adjuvante organosiliconado e um fertilizante foliar a base de manganês sobre a eficácia do inseticida imidaclopride no controle de *Triozoida limbata* em goiabeiras. A parcela experimental foi considerada com quatro árvores seguidas na mesma linha de cultivo, subdividida em 4 quadrantes. O experimento foi conduzido em delineamento de blocos ao acaso, em parcelas subdivididas, com quatro repetições. Os tratamentos foram T1 - Imidaclopride (Imid.); T2 - Imid. + Copolímero de poliéter-polimetil-siloxano (Sil.); T3 - Imid. + $MnSO_4$; T4 - Imid. + Sil + $MnSO_4$; T5 - Controle (sem aplicação). Características físico-químicas, deposição sobre as folhas e perdas para o solo, além da porcentagem de infestação do psilídeo na goiaba e o número de ninfas foram avaliados. A adição de fertilizante foliar na mistura reduziu o pH e a tensão superficial e aumentou a condutividade elétrica e a viscosidade das soluções inseticidas. O adjuvante de siliconado reduziu a tensão superficial e aumentou a viscosidade e o pH. A mistura em tanque de adjuvante organosiliconado e fertilizante foliar a base de manganês não influenciam o nível de eficácia do inseticida.

Palavras-Chave: Psilídio da goiaba; características físico-químicas; neonicotinóides; fertilizante foliar; Organosiliconado

1 INTRODUCTION

The guava tree (*Psidium guajava* L.) stands out among the Brazilian tropical species, mainly by its flavor and nutritional value. To raise the quality of the product and thereby expand the production, the growers must overcome some obstacles as orchard conduction, problems with fertilization, application technologies as well as the high number of diseases and pests. One of the main problems for guava production is an insect, known as the guava psyllid (*Triozoida limbata* Enderlein - Hemiptera: Triozidae) (Galli et al. 2014; Barbosa and Lima, 2010; Souza Filho and Costa, 2009).

The characteristic symptom of guava psyllid attack is the winding from the edges of the leaves, where colonies of nymphs stays. With this attack the leaves could fall, compromising the production (Barbosa et al., 2001; Gallo et al., 2002). According to Colombi and Galli (2009) the importance of this psyllid has probably increased because of the adopted production system, with more irrigation and tree pruning, that favors the psyllid population growth because of the abundant amount of new sprouts.

“Paluma” is one of the most used cultivars in the Brazilian orchards mainly because it presents capacity to produce fruits even to industry and for *in natura* use (Farias et al., 2017). This cultivar does not present resistance to the attack of guava psyllid that became one of the main problems for its production (Barbosa and Lima, 2010).

The use of pesticides is frequent during the tree cycle. This leads growers to choose tank mixture of pesticides, and this have become a common practice in the Brazilians fields, in order to keep the field productivity and reduce the application cost. The main problem is the uncertain effects that each mixture of different products can cause on the application (Gazziero et al., 2015).

Neonicotinoids, which are remarkably effective insecticides against sucking insect pests have been shown effectively control to the guava-psyllid before (Barbosa et al., 2001), does not present the same effect over this pest, as described by Lima and Gravina (2009) that found an inefficacy of this product on high-density level of infestation after some time. Besides the efficiency decrease of the products, the association of different compounds within the spray tank could have influence on the efficacy of these products.

Tank mixture has been a very common practice in agriculture, especially with the addition of adjuvants and foliar fertilizers. However, the effect of these blends were not well known. Physical-chemical properties are altered with these mixtures and may influence the efficacy of plant health products.

The penetration and physiological effect of leaf-applied nutrient sprays involves a series of intricate mechanisms ranging from the mode of application, to the physical-chemical characteristics of the solution, the prevailing environmental conditions or the target plant species. There are many processes involved, which make difficult the development of new strategies to optimize the efficiency of foliar sprays under different growing conditions and diverse plant species (Fernandez and Eichart, 2009).

The adjuvants added to the mixture to enhance the efficiency could act in different ways. They could improve spreading of the droplet and the wetting of the spray mixture over the target (Cunha, Bueno and Ferreira 2010), as well as influence the penetration through the cuticle (Wang and Liu, 2007). Depending of the adjuvant composition and formulation, they could affect physical-chemical characteristics, mainly pH, surface tension and viscosity (Cunha and Alves 2009).

Therefore, the objectives of this study were to evaluate the effect of tank mixture of an organosilicon adjuvant and manganese foliar fertilizer on the imidacloprid insecticide efficacy over the *Triozoida limbata* control in guava trees.

2 MATERIAL AND METHODS

2.1 Experimental Site

The present study was carried out in duplicate (two periods of application) in a guava orchard (*Psidium guajava* L.), “Paluma” cultivar, at the experimental farm “Água Limpa” (19° 6'16,49"S and 48°20'54,38"W), belonging to the Federal University of Uberlândia (UFU), Uberlândia - MG - Brazil. According to Köppen classification, the area is characterized as Aw (tropical, hot humid area with cold and dry winter) with an altitude of 795 m.

It was selected an area of production (nine years old), with 80 plants, spaced in 5.0 m between cultivation lines and 3.0 m between plants. The experimental plot was considered with four trees followed in the same cultivation line subdivided into 4 quadrants (Q1, Q2, Q3 and Q4). Treatments were applied with applications of 600 L ha^{-1} at 0.46 km h^{-1}. Q1 and Q3 were allocated in the same direction as the cultivation line, Q2 and Q4 were perpendicular (Figure 1).

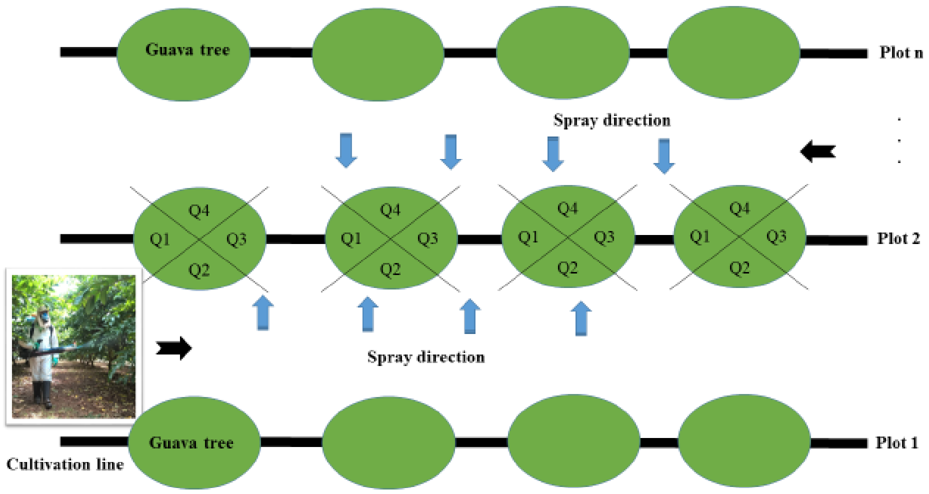

Figure 1. Spray direction through the plot

The first period (1st application) was conducted in 2017/2018 harvest, on December 14th 2017, a period of high infestation of guava psyllid. The second period on April 13th 2018 (2nd application), after harvesting the fruits, the experiment was repeated in the same area, following the same methodology.

2.2 Treatments

Treatment solutions were prepared with one manganese salt (manganese sulfate – $MnSO_4$), one adjuvant (polyether-polymethyl siloxane copolymer) and one insecticide (Imidaclopride) at the Agricultural Mechanization Laboratory (LAMEC), from the Federal University of Uberlândia (UFU). The products specifications are in Table 1.

Table 1. Products Specifications

Product	Active ingredient	Function	Concentration	*Formulation	Dose
Provado® SC 200	Imidaclopride (Imid)	Insecticide	200 g L^{-1}	SC[1]	2.5 mL $plant^{-1}$
Break Thru®	Polyether-polymethyl siloxane copolymer (Sil.)	Adjuvant	1000 g L^{-1}	SC[2]	0.1 % $v\ v^{-1}$
Manganese sulfate	Manganese sulfate ($MnSO_4$)	Foliar fertilizer	30 %	PW	0.05 %

*SC[1] – Suspension concentrate; SC[2] – Soluble concentrate; PW – Powder;

Treatments were T1 – Imidaclopride (Imid.); T2 – Imid. + Polyether-polymethyl siloxane copolymer (Sil.); T3 – Imid. + $MnSO_4$; T4 – Imid. + Sil. + $MnSO_4$; T5 – Control (no application).

2.3 Experiment conduction

For the applications, a Stihl® SR450 motorized pneumatic backpack sprayer with a 14 L tank and a two-stroke single cylinder engine of 2900W power was used. This machine does not use a hydraulic nozzle. The droplets are formed by action of the wind and in accordance with the setting of the orifice, which is the output of the spray. A flow rate of 1.45 L min^{-1} was used and the engine was half accelerated in order to cause less drifting and not overload it.

The treatments application happens perpendicular at the cultivation line (Q2 and Q4 receive direct application) on both sides of the tree (Figure 1), and at distance of approximately 1.5 m between the sprayer and the tree. To avoid plots contamination was used during the application plastic canvas that covered the adjacent area. After the application, the collected samples (leaves and petri dishes) were analyzed at the Laboratory of Agricultural Mechanization.

The environmental conditions at the time of the applications monitored during the experiments on the first period were: temperature (°C) between 23.7 - 27.5; humidity (%), 60.5 - 70.0; and wind speed (km h^{-1}) 4.5 - 11.7. On the second period, the temperature (°C) vary between 23.9 - 29.1; humidity (%), 55.6 - 75.6; and wind speed (km h^{-1}) 0.1 – 5.6.

2.4 Evaluations

2.4.1 Physical-chemical evaluations

Different tank mixtures were prepared with pesticide to evaluate the physical-chemical characteristics: density, pH, electric conductivity (EC), viscosity (Visc.) and surface tension (ST). In the ways of comparison, it was evaluated distilled water. The evaluations were done as described elsewhere (CUNHA et al., 2010). The evaluations of physical-chemical properties were realized at LAMEC of UFU.

2.4.2 Application technology evaluation

For the evaluation of the application technology each plot consisted of four plants, and every useful plant was subdivided into four quadrants. Only quadrants (subplots) Q2 and Q4 were direct targets during the applications (Figure 1).

To evaluate the deposition and the losses to the soil, a marker consisting of the food dye Brilliant Blue (Federal Food, Drug and Cosmetics Act as FD&C Blue Nº. 1) was added to the application mixture at a fixed concentration of 2000 mg L^{-1} mixture for detection by absorbance spectrophotometry. The colouring was quantified by absorbance at 630 nm using a spectrophotometer.

Two central plants formed the useful area of each plot, from which two leaves per quadrant were collected, resulting in 16 leaves per plot. These leaves were collected immediately after the applications from the middle third of the plants in the middle part of the canopy.

To evaluate the losses of the spray mixture to the soil, two sets of petri dishes consisting of a cover and a bottom dish were placed on the ground under the canopy of the second guava tree in each plot. The dishes were placed 20 cm from the plant's trunk that each dish was located in a quadrant of the plant. The bottom dishes of each set (150 cm^2) were arranged in quadrants Q1 and Q3, while the covers (170 cm^2) were placed in quadrants Q2 and Q4.

After spraying, the dishes were collected and stored for later quantification of the marker. In the laboratory, 100 mL of distilled water was added to each plastic bag containing the guava tree leaves. A quantity of 30 mL of distilled water was added to the petri dishes, which were closed and shaken for 30 s to homogenize the dye present in the samples.

The liquid was then removed and transferred to plastic cups, which were stored for 24 h in a refrigerated location away from light, for subsequent absorbance readings in a spectrophotometer.

The weight of the dye retained in the leaves of the guava tree was determined based on the initial concentration of the spray mixture, the concentration of the samples and the dilution volume. The total amount deposited was divided by the leaf area of each sample to obtain the amount (µg) of dye per cm^2 of leaf area. For the losses to the soil, the same calculation was performed, but using the area of the dishes. The leaf area was measured with an LI-COR Environmental - LI-COR Biosciences, model LI-3100.

2.4.3 Pest evaluation

On the day before the first application, the psyllids (*Triozoida limbata*) in the area were sampled, to check the level of pest infestation. The evaluations were done at 7^{th}, 12^{th} and 14^{th} days after the application (Daa).

The two central trees from the plot were considered for efficacy sampling, as the first and the last tree considered as borders. The damage threshold of the guava psyllids was when 30% of the leaves justified spraying for pest management in the area. The samples were taken from the middle third of the central guava trees. During this evaluation, one branch per quadrant was marked with "non-woven" tape for each of the central trees of the plot such that the same branch was used in all subsequent evaluations. The percentage of psyllid-damaged leaves was verified using the last two pairs of leaves in this branch.

In addition, one leaf per quadrant was collected from each central tree, always from the last two pairs of leaves of each branch. Then, with the aid of a digital microscope (Dino-lite pro model: AM – 413ZT) with 200x magnification, the number of psyllid nymphs was counted (Fig 2) on each leaf, and the mean of the plot was calculated.

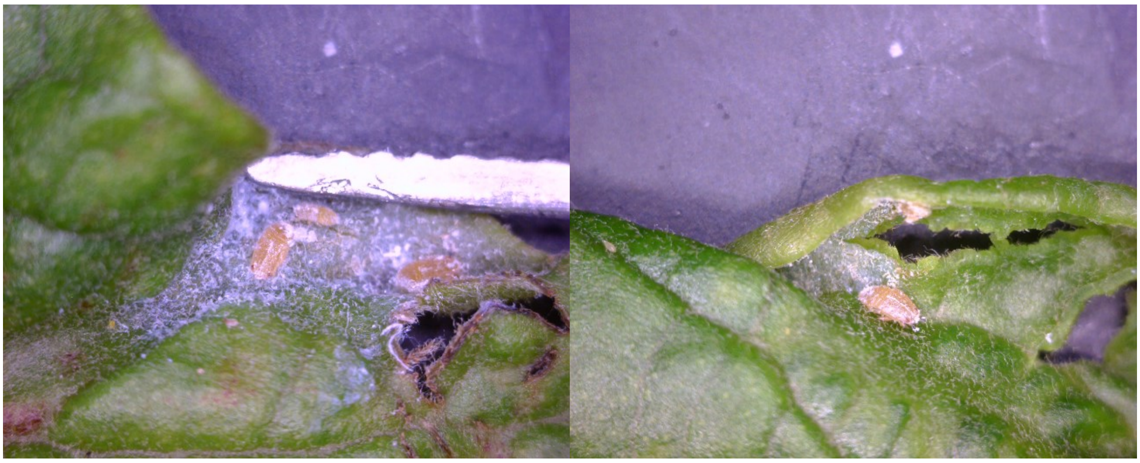

Figure 2. Guava psyllid nymph (*Triozoida limbata*) and caractheristic sympton of their attack

2.5 Experimental design and statistical analysis

The experiment was conducted in a casually delineated blocks with split-plot, with five treatments and four replications. The treatments were the plots and the quadrants (Q1, Q2, Q3 and Q4) constituted the subplots. The obtained data was submitted to normality test of normal distribution of errors (Shapiro Wilk) and homogeneity of variances from Levene, in 0.01 of significance.

The "F" test was performed to determine levels of significance of 0.05 and 0.01 for the analysis of variance. When these tests were significant, the averages were compared with the Scott-Knott test at 0.05 level of probability. When necessary data was transformed by $\sqrt{(x+1)}$.

3 RESULTS AND DISCUSSION

3.1 Physical-chemical evaluations

The physical-chemical characteristics of the treatments changed according to each product added. The adjuvant did not change EC in the treatment with only insecticide and provided a small increase in pH. On the other hand, the foliar fertilizer reduced the pH and increased EC expressively.

But then, the values of density increased according to the addiction of products in the mixture and the higher values were achieved in the mixture with all products (Table 1). However, the magnitude of the changes was low.

The mixtures also influenced the surface tension. All the products reduced it in relation to water, with emphasis on the foliar fertilizer and the adjuvant, which resulted in the lowest values. According to Iost and Raetano (2010) the silicon adjuvants were more efficient in reducing the surface tension values than other adjuvants. This reduction promotes a greater spread of the droplets on the target, which can favor its absorption. Still, extremely low values of surface tension can lead to run-off.

Regarding viscosity, the addition of the fertilizer and the adjuvant to the insecticide increased its value and this may influence the spray droplet spectrum. Higher viscosity of the spray results in larger droplet sizes. The addition of ions in the solutions had directly influence over these characteristics. The foliar fertilizer had the potential to decrease surface tension, without the use of the adjuvant. Andrade et al. (2013) found that some of these characteristics, mainly the pH, were influenced by the addition of some foliar fertilizers.

Table 1. Physical-chemical characteristics of the treatments

Treatments	Density ($g\ L^{-1}$)	pH	EC ($\mu S\ cm^{-1}$)$^{+}$	Visc. ($mPa\ s^{-1}$)	ST ($mN\ m^{-1}$)
Imid	1.026 C	6.32 C	4.00 D	0.94 E	50.75 B
Imid+ Sil.	1.029 B	7.27 A	4.75 D	1.06 B	25.50 C
Imid+ $MnSO_4$	1.034 A	4.55 D	1729.00 B	1.02 C	26.50 C
Imid+ Sil. + $MnSO_4$	1.034 A	4.30 E	1961.50 A	1.13 A	23.75 D
Water	1.024 D	6.85 B	16.25 C	0.99 D	71.50 A
CV	1.31	2.55	1.91	0.91	3.07
F	15242.222*	329.026*	14700.377*	230.179*	1199.713*
Flevene	4.785^{ns}	3.607^{ns}	1.877^{ns}	0.458^{ns}	0.769^{ns}
SW	0.956^{ns}	0.920^{ns}	0.934^{ns}	0.946^{ns}	0.939^{ns}

$^{+}$EC: data transformed $\sqrt{(x+1)}$; CV – Coefficient of variation; F- values of calculated F for different treatments. SW – Shapiro Wilk test. ^{ns};* - not significant; significant at 0,05.; Means followed by the same letter do not differ according to Scott Knott ($p \leq 0.05$).

3.2 Application technology

From the analyzed variables for application technology, foliar deposition was significant ($P<0.05$) for treatments and quadrants only for the first period of application. This evaluation did not present any interaction between the treatments and the quadrants (Table 2).

By the way, losses to the soil were significant for the interaction between the treatments and the quadrants for both applications.

Table 2. ANOVA summary for application technology

	1st application		**2nd application**	
	Deposition	**Losses to the soil**	**Deposition**	**Losses to the soil**
Ftreat	4.776*	1.822 ^{ns}	2.031 ^{ns}	4.473*
Fquad	7.719*	1.723 ^{ns}	0.754 ^{ns}	5.839*
Ftreat*quad	0.345^{ns}	2.416*	0.715 ^{ns}	2.991*
Flevene	2.234 ^{ns}	1.813 ^{ns}	2.286 ^{ns}	2.077 ^{ns}
SW	0.982 ^{ns}	0.975 ^{ns}	0.974 ^{ns}	0.948 ^{ns}

F- Values of calculated F for different treatments. SW – Shapiro Wilk test. ^{ns};* - not significant; significant at 0.05.

The tracer deposition in the first application was higher in the treatment only with insecticide, differently from the other treatments that presented the same deposition standard (Table 3).

Table 3. Foliar deposition of tracer ($\mu g\ cm^{-2}$) after treatment applications (First application)

Treatments	Deposition (µg cm^{-2})
Imid	10.33 A
Imid+ Sil.	7.08 B
Imid+ $MnSO_4$	7.61 B
Imid+ Sil. + $MnSO_4$	5.54 B
CV_t	47.80

CV - Coefficient of variation; t – values of treatment; Means followed by the same letter do not differ according to Scott Knott ($p \leq 0.05$).

In Table 1 the values of surface tension were drastically reduced when the products were added with the insecticide. When the leaves were sprayed, the droplets could stay over the leaf, adhered, spread or even runoff. According to Van Zyl et al. (2010) depending of the surfactant concentration the values of surface tension could become lower and them may cause excessive spreading with droplet runoff. This could justify the lower values of deposition in the treatments that had more products than the insecticide.

The deposition of tracer was higher in quadrant 2 and 4 as expected (Table 4). Mainly because the direction of application (perpendicular to the direction of the cultivation line) and the leaves overlay of quadrant 1 and 3 from the border plants. Tavares et al. (2017) found similar results when evaluated electrostatic application in guava trees, being that the quadrants that received direct application had more deposition than the others that did not receive it.

Table 4. Foliar deposition of tracer (µg cm^{-2}) on each quadrant (First application)

Quadrant	Deposition (µg cm^{-2})
1	6.24 B
2	11.08 A
3	4.85 B
4	8.39 A
CV_q	53.08

CV - Coefficient of variation; q– values of quadrant; Means followed by the same letter do not differ according to Scott Knott ($p \leq 0.05$).

On the first application, the treatments presented almost the same standard from spray losses to the soil in all four quadrants, except the lower loss on quadrant 2 for the treatment with all products and the treatment with Imid + $MnSO_4$, which presented higher losses in the same quadrant (Table 5). Then again, for the second application Imid +Sil. and the treatment with all products presented similar losses to the soil in all quadrants. The treatments with only the insecticide had more losses in quadrant 1, by the way when the adjuvant was added the losses became higher on quadrants 3 and 4 (Table 5).

Table 5. Spray loss (μg cm^{-2}) to the soil (1st and 2nd application)

Treatments	Quadrants			
1st application				
	1	**2**	**3**	**4**
Imid	0.52 Aa	0.51 Ab	0.54 Aa	0.68 Aa
Imid+ Sil.	0.63 Aa	0.26 Ab	0.30 Aa	0.56 Aa
Imid+ $MnSO_4$	0.83 Aa	0.81 Aa	0.46 Aa	0.65 Aa
Imid+ Sil. + $MnSO_4$	0.45 Aa	0.17 Bb	0.78 Aa	0.53 Aa
CV_t	77.31			
CV_q	44.79			
2nd application				
	1	**2**	**3**	**4**
Imid	1.08 Aa	0.46 Ba	0.74 Ba	0.58 Ba
Imid+ Sil.	0.38 Bb	0.19 Ba	0.89 Aa	0.68 Aa
Imid+ $MnSO_4$	0.22 Ab	0.29 Aa	0.57 Aa	0.48 Aa
Imid+ Sil. + $MnSO_4$	0.21 Ab	0.16 Aa	0.25 Ab	0.17 Aa
CV_t	88.71			
CV_q	49.44			

CV - Coefficient of variation; t – values of treatment; q– values of quadrant; Means followed by the same letter, uppercase in line and lower case in column, do not differ according to Scott Knott ($p \leq 0.05$).

The spray losses values were similar as found by Tavares et al. (2017) when they evaluated standard application in guava trees with the same equipment and spray volume.

3.3 Pest evaluation

From the analyzed variables for pest evaluation (nymph number and infestation) the results were significant ($P<0.05$) according with the different evaluation period as showed in Table 6.

On the first application, the psyllid infestation was different according to each evaluated quadrant. The percentage of infestation 7 Daa was higher on quadrant 1 and 3. Different from the second application that the % of infestation was higher on quadrant 2 and 4 (Table 7). These results have a relation with the deposit of tracer in the quadrants (Table 4), showing that, in this case the quadrants that received more deposit presented a reduction of the percentage of infestation.

Table 6. ANOVA summary for pest evaluation

Nymph number (average)	
1st application	**2nd application**

	0 Daa	7 Daa	12 Daa	14 Daa	0 Daa	7 Daa	12 Daa	14 Daa
Ftreat	1.694^{ns}	0.797^{ns}	1.014^{ns}	3.248*	1.379^{ns}	3.001^{ns}	5.578*	10.709*
Fquad	0.967^{ns}	0.137^{ns}	3.011*	7.121*	6.648*	5.856*	1.989^{ns}	2.498^{ns}
Ftreat*quad	2.070*	0.904^{ns}	1.012^{ns}	0.880^{ns}	1.656^{ns}	0.834^{ns}	0.482^{ns}	0.640^{ns}
Flevene	2.057^{ns}	2.700^{ns}	1.419^{ns}	0.836^{ns}	1.678^{ns}	2.359*	5.640*	6.871*
SW	0.947*	0.985^{ns}	0.980^{ns}	0.948*	0.972^{ns}	0.971^{ns}	0.815*	0.915*

Psyllid infestation (%)

	1st application				**2nd application**			
	0 Daa	**7 Daa**	**12 Daa**	**14 Daa**	**0 Daa**	**7 Daa**	**12 Daa**	**14 Daa**
Ftreat	0.917^{ns}	2.248^{ns}	8.917*	17.593*	0.422^{ns}	4.913*	4.608*	8.004*
Fquad	0.105^{ns}	4.056*	1.947^{ns}	0.678*	0.717^{ns}	7.686*	2.400*	2.560^{ns}
Ftreat*quad	1.369^{ns}	0.574^{ns}	1.113^{ns}	1.202^{ns}	1.111^{ns}	1.202^{ns}	1.403^{ns}	1.395^{ns}
Flevene	1.200^{ns}	2.059^{ns}	2.548*	2.007^{ns}	1.718^{ns}	1.532^{ns}	2.221*	1.540^{ns}
SW	0.945*	0.979^{ns}	0.972^{ns}	0.971^{ns}	0.972^{ns}	0.975^{ns}	0.973^{ns}	0.951*

F- Values of calculated F for different treatments. SW – Shapiro Wilk test. ^{ns}; * - not significant; significant at 0.05.

On the second period of the experiment, the plants present reduced number of leaves because of the climate and the overlay of the branches of the neighbor plants on quadrants 1 and 3, that did not happen in the first period because the size of the trees (Table 7).

Table 7. Psyllid infestation (%) in different tree quadrants

Quadrants	**1ª application**			
	0 daa	**7 daa**	**12 daa**	**14 daa**
1	37.50	48.75 B	36.25	27.50
2	32.50	26.25 A	33.75	35.00
3	37.50	47.50 B	40.00	27.50
4	35.50	22.50 A	20.00	22.50
CV_t	84.75	70.91	59.76	63.25
CV_q	68.97	72.71	86.00	88.02
Quadrants	**2ª application**			
	0 daa	**7 daa**	**12 daa**	**14 daa**
1	42.50	27.50 A	23.75 A	22.50
2	55.00	58.75 B	37.50 B	35.00
3	52.50	22.50 A	21.25 A	16.25
4	52.50	41.25 B	37.50 B	28.75
CV_t	73.11	46.05	90.89	69.13
CV_q	57.85	69.83	83.91	68.02

CV - Coefficient of variation; t – values of treatment; q– values of quadrant; F- values of calculated F for different treatments. Means followed by the same letter do not differ, in the column, according to Scott Knott ($p \leq 0.05$).

Different from infestation, the number of nymphs presented higher values on quadrant 2 and 4 on the first period of application (Table 8).

On the second application, on 0 Daa, the distributions of nymphs were similar in all quadrants. However, at 7 Daa the number of nymphs reduced in quadrants 1 and 3 and increased in 2 and 4. On 12 Daa and 14 Daa the number of nymphs reduced in comparison to the previous evaluation but was not statistically significant (Table 8).

Table 8. Psyllid Nymph (average) according to each different tree quadrant

Quadrants	1st application			
	0 daa	**7 daa**	**12 daa**	**14 daa**
1	3.25	2.05	2.60 A	2.95 A
2	2.10	2.45	5.80 B	8.60 B
3	2.10	2.00	2.85 A	2.55 A
4	2.25	2.40	4.15 B	6.70 B
CV_t	73.24	79.14	57.89	68.85
CV_q	75.12	25.16	71.31	57.50
Quadrants	**2nd application**			
	0 daa	**7daa**	**12 daa**	**14 daa**
1	10.35	2.25 A	0.70	1.45
2	7.90	16.50 B	2.40	3.00
3	7.79	3.90 A	0.65	0.85
4	3.35	13.90 B	2.35	2.00
CV_t	64.62	69.27	59.79	68.88
CV_q	53.12	53.06	86.00	72.10

CV - Coefficient of variation; t – values of treatment; q– values of quadrant; F- values of calculated F for different treatments. Means followed by the same letter do not differ, in the column, according to Scott Knott ($p \leq 0.05$).

Marcelino and Barbosa (2016) found that *T. limbata* adults showed a moderate to highly aggregated distribution in all phases of guava culture, independently of the average size of the population, which could justify the higher number of nymphs in quadrants 2 and 4 that had more leaves.

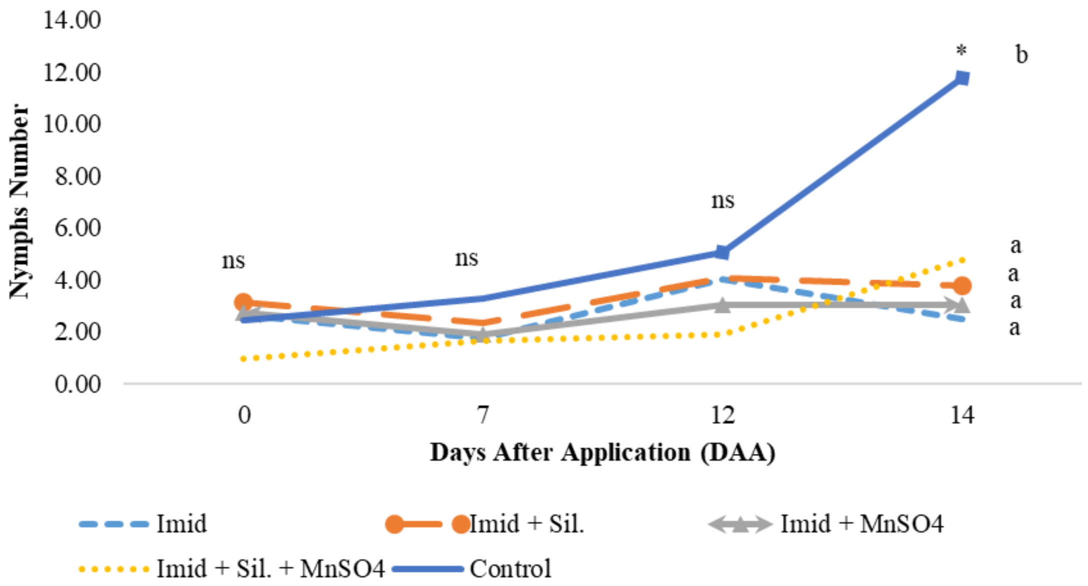

Figure 3. Average nymph number after the treatment applications (1st period). ns;* - not significant; significant at 0,05.; Means followed by the same letter do not differ according to Scott Knott ($p \leq 0.05$).

According to Figure 3, the number of nymphs were similar after the treatments application. On 14 Daa the number of nymphs had increased on the control treatment differing from the others that had the same average, presenting that the insecticide had effect over the insects until this time.

On the second application, the number of nymphs fluctuated until the 12 Daa. Only on 14 Daa that the treatments presented difference in control. On this application the number of nymphs had been reduced from the treatments with the insecticide, except the mixture of it and the foliar fertilizer, that presented a difference between the other ones and the control too (Fig 4).

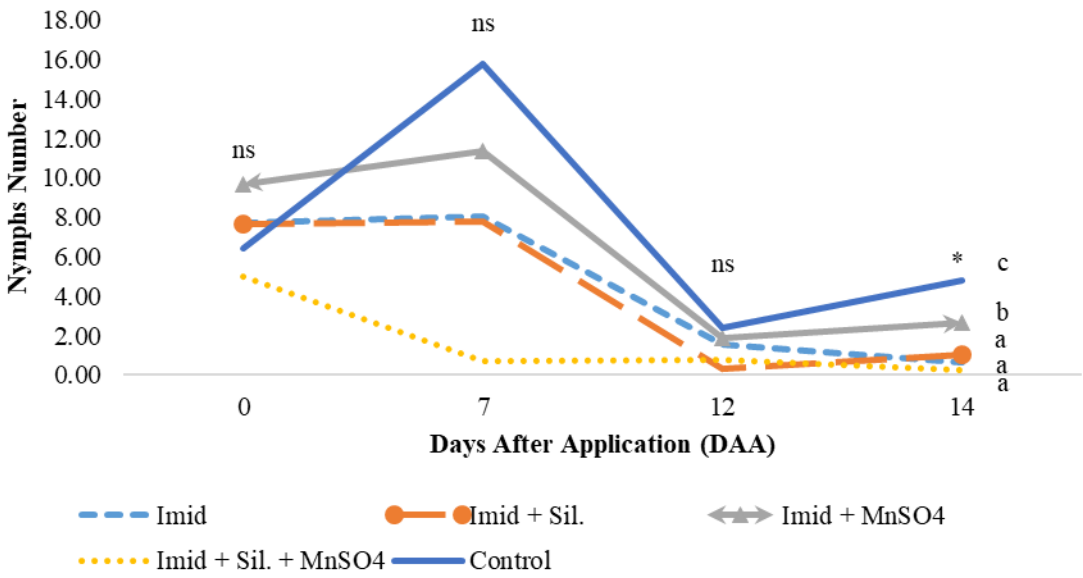

Figure 4. Average nymph number after the treatment applications (2nd period). ns;* - not significant; significant at 0.05.; Means followed by the same letter do not differ according to Scott Knott $p \leq 0.05$.

Galli et al. (2014) found that cv "Paluma" and "Rica" where the most attacked by the psyllid comparing with different accesses, some commercials and others in test. The percentage of damage were higher than 50% during all the experiments.

The damage threshold of 30% was achieved and the applications were necessary on both periods (Fig 5 and 6). These levels reduced on the 12 and 14 Daa, except for the control (Fig 5) on the first period and starting from 7 until 14 Daa on the second application (Fig 6). On both situations, the damage threshold was reduced above the recommended to another application, which justify only one in each period.

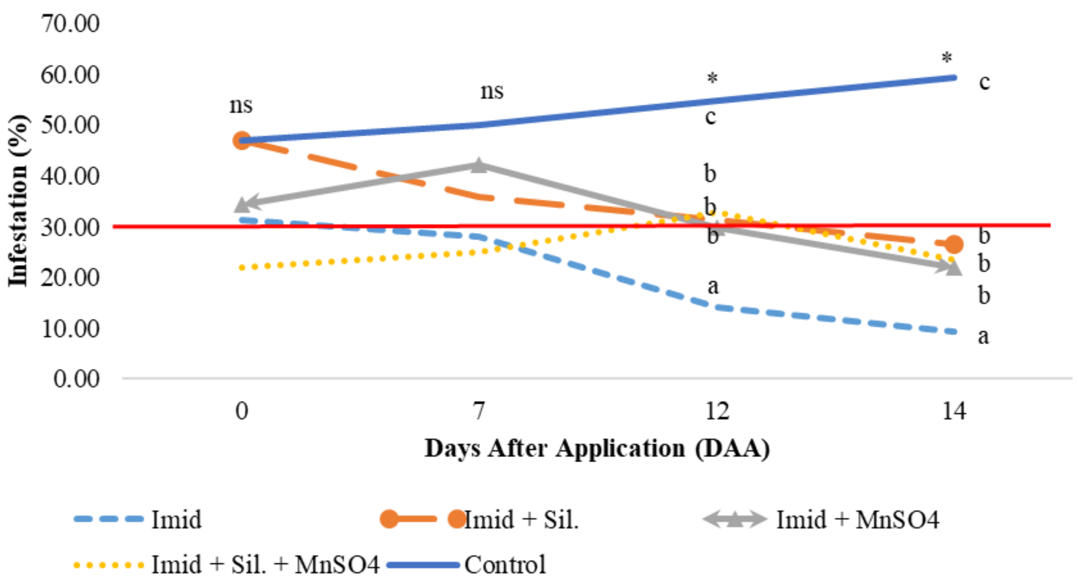

Figure 5. Leaves infested (%) by psyllid in guava trees (1st period).ns;* - not significant; significant at 0.05.; Means followed by the same letter do not differ according to Scott Knott ($p \leq 0.05$).

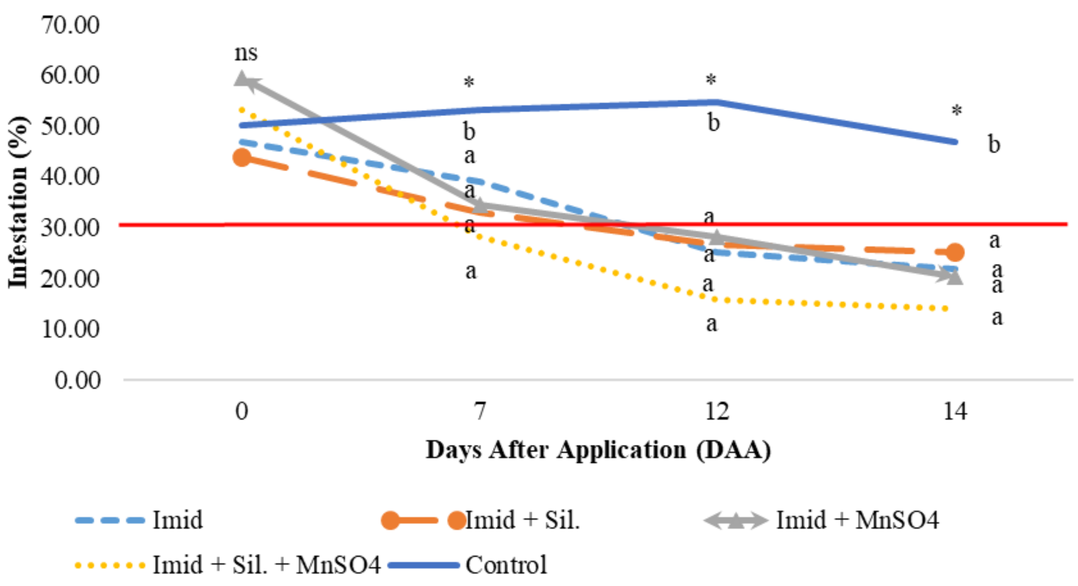

Figure 6. Leaves infested (%) by psyllid in guava trees (2nd period).ns;* - not significant; significant at 0.05.; Means followed by the same letter do not differ according to Scott Knott $p \leq 0.05$.

The first application all treatments reduced the % of infestation but the treatment only with insecticide reduced more than the others (Fig 5). This does not happen on the second application, when all the treatments reduced the infestation to the same level, becoming only different from the control (Fig 6). As we can see in Table 3, the foliar deposition of the treatment with only insecticide was higher than the others, justifying this difference between the treatments in the first application.

When applied over high density levels (higher than 50%) and with an interval of 15 days between applications, the imidaclopride insecticide did not reduced the infestation levels above the damage threshold (Lima and Gravina, 2009). Tavares et al. (2017) found similar efficacy to our results over the guava psyllid control with the same insecticide, reducing the threshold above the recommended.

4 CONCLUSION

The addition of foliar fertilizer on the mixture reduced the pH and surface tension and increased the electric conductivity and viscosity of the insecticide solutions. The silicon adjuvant reduced the surface tension and increased the viscosity and the pH.

The quadrants that received direct application (2 and 4) presented higher spray deposition. All the treatments and quadrants presented almost the same spray losses to the soil.

The number of nymphs as well as the infestation level decreased with the treatment's applications. The tank mixture of organosilicon adjuvant and manganese foliar fertilizer did not influence the efficacy level of the insecticide.

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