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The Impact of a Non-ionic Adjuvant to the Persistence of Pesticides on Produce Surfaces

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A Thesis Presented

By

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Abstract

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February 2024

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Adjuvants can enhance the performance of the pesticide active ingredients in many ways including decreasing surface tension and reducing evaporation. Understanding how adjuvants effect pesticide behavior (e.g., surface persistence) is crucial for developing effective pesticide formulations, as well as facilitating the development of effective approaches to reduce pesticide residues from the surface of fresh produce post-harvest. The objective of this study is to investigate the effect of a non-ionic surfactant, Surf-Ac 910, on the persistence of two model pesticides, thiabendazole and phosmet on apple surfaces. The result shows that the addition of Surf-Ac 910 increased both the maximum wetted area and evaporation rate of thiabendazole, a systemic pesticide, and phosmet, a non-systemic pesticide. Utilizing surface-enhanced Raman spectroscopy to explore the surface and penetrative behaviors of thiabendazole and phosmet revealed that the addition of Surf-Ac 910 influenced the Raman signal of pesticides as well. The addition of Surf-Ac 910 decreased the Raman signal intensity when added to phosmet but did not affect the Raman signal intensity when added to thiabendazole. In terms of penetration, the addition of Surf-Ac 910 did not affect the penetration depth of phosmet but slightly increased the penetration depth of thiabendazole. These findings were true for both short-term, 40 minutes, and long-term, 3 days, exposure. Next, the effects of adjuvants on the removal of pesticide residues were investigated. Common household materials, such as baking soda, were effective at removing surface pesticide residues. After testing a variety of baking soda concentrations and starch granules, 2% baking soda and 2% corn starch were found to be the most effective baking soda concentration and starch granule respectively. 2% corn starch was the most effective removal method overall, with 99% of pesticide with/without adjuvant removed in just 5 minutes of wash time. Overall, this study demonstrated that although adjuvant Surf-Ac 910 could affect the surface persistence of pesticides, washing with common household materials such as 2% corn starch can be used as an effective, safe, and economic way to reduce pesticide exposure through fresh produce.

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Chapter 1: Introduction and Background Information

Pesticide and Adjuvant Background Information

Pesticides are an important and necessary part of agriculture, as farmers apply pesticides to protect their crops from various pests that can both destroy crops and have negative effects on human health (Food and Agriculture Organization of the United Nations, 2017; Savary et al., 2019). Pesticides are critical to meet the increasing global demand for food, as without the use of pesticides, it is estimated that fruit yields would drop by 78%, vegetable yields by 54%, and cereal productions by 32% (Chen et al., 2023; Tudi et al., 2021). However, there has been growing concern over the negative health effects of pesticide residues left on produce and consumed (Dhankhar 2023; Yang et al., 2016). For example, it has been shown that consumption of the insecticide chlorpyrifos is linked to developmental problems in children (Dhankhar 2023). Due to these concerns, studying pesticides and their behaviors is a key part of understanding how to mitigate pesticide residues. While there has been a lot of research done on the behaviors of pure pesticides, there have not been a lot of studies done on pesticides combined with adjuvants (Al-Taher et al., 2023; Wang et al., 2022; Kumar et al., 2017). In real-world application, pesticide solutions have active and inert ingredients (Tu et al., 2023). The active ingredient is the chemical that controls the pest, while the inert ingredients help the pesticide solution performance (Krogh et al., 2003; Kaczmarek et al., 2021; Wang et al., 2022). An adjuvant is an inert ingredient, as an adjuvant is any substance that enhances the performance of the pesticide solution (Krogh et al., 2003; Kaczmarek et al., 2021; Wang et al., 2022). Adjuvants are an important factor to consider since they can dramatically change the pesticide behavior, which impacts how that pesticide residue can be removed post-harvest (Du et al., 2023). Pesticides are divided into two main categories based on their behaviors; systemic and non-systemic pesticides (Yang et al., 2016; Goulson 2013). Systemic pesticides can penetrate plant tissue, while non-systemic pesticides sit on the surface of the plant and do not penetrate plant tissue (Yang et al., 2016; Goulson 2013). Adjuvants can affect these traits, and if mixed with an adjuvant, a non-systemic pesticide could potentially have penetration behavior that would otherwise not be possible (Du et al., 2023). Developing an understanding of how adjuvants affect pesticide solutions will allow future researchers to find the best methods of removal for pesticide residues and better protect human health.

Significance

This study is significant for several reasons including health concerns over pesticide use. While pesticides are used to protect crops from various pests and diseases, the effects of pesticides are not always selective to just the pest (Ashraf et al., 2023). Exposure to pesticides and pesticide residues can pose a risk to human health, especially as pesticide use is widespread (Ashraf et al., 2023; Fernandes et al., 2023). Over 1 billion pounds of pesticides were applied in the United States in 1999 (usgs.gov). Due to the high usage, the population is exposed to pesticide residues through contaminated food and water, application of pesticides in public spaces, pesticide use at home, and occupational exposures (Damalas 2011). For the purposes of this study, we are focused on pesticide residues found on food. Exposure through contaminated food represents an indirect exposure to pesticide residues that is characterized by long-term low-level exposure (Hu et al., 2015).

Two of the major public concerns regarding pesticide residues are the possibility of pesticides being carcinogenic and neurotoxic. While it is important to note that there is no concrete evidence linking pesticide exposure to cancer, there have been studies conducted that indicate a connection between some pesticides and cancer (Akoto 2015; Garry 2003; Bhatia et al., 2005). One example is that organochlorine pesticides have been linked to conditions such as Non-Hodgkin's Lymphoma (Chen et al., 2020). In terms of neurotoxicity, it is thought that low-level exposure can result in mild symptoms such as headache, dizziness, fatigue, weakness, and nausea (Pope et al., 2005). Dietary intake is one of the most common routes of low-level pesticide exposure as people consume pesticides residues left on produce post-harvest (Fenske et al., 2002; Clayton et al., 2003). Pesticide exposure through dietary intake is especially prevalent in children, who have a higher food consumption than adults (Faustman et al., 2000; Kroes et al., 2002). This puts children at a higher risk, and childhood cancer is associated with the consumption of foods contaminated with pesticides (Akoto 2015; Garry 2003; Bhatia et al., 2005). A better understanding of how pesticides behave, as well as, how to remove pesticides residues from the surface of produce is important for reducing the exposure of pesticides to the public.

Even without proven evidence for pesticides being carcinogens or neurotoxic at low levels, the concern has created a demand for better ways to remove pesticide residues from food (Yang et al., 2017). This has led to investigations into how effective different washing methods are, including water and synthetic detergents. Interestingly, previous studies found natural and household cleaners such as baking soda are more effective at removing pesticide residues than synthetic detergents (Yang et al., 2017). Products like baking soda are also desirable because they are safe for human consumption, easy to access, and safe for the environment (Yang et al., 2017). This study will be further exploring the efficacy of baking soda as a removal method, as well as other household ingredients such as starches.

Innovation

This study is innovative for several reasons. For one, most studies conducted on pesticides, only study pesticides as pure analytical compounds. This provides a good understanding of how the active ingredient works but does not give any insight into the numerous inert ingredients that are often added into the pesticide solution. These inert ingredients, or adjuvants, are ingredients that are added to enhance the stability and efficacy of the pesticide. There are three kinds of adjuvants, each with unique behaviors and impact on the pesticide performance (Du et al., 2023; Appah et al., 2020). The three kinds are surfactants, oils, and acidifiers or buffers (Du et al., 2023; Appah et al., 2020). Not only can adjuvants impact the performance, but they can also change the behaviors of pesticides. Due to this, without studying the effects of adjuvants, we do not clearly understand how pesticides work and how to best remove them post-harvest. Therefore, the aim of this experiment is to investigate the impact of a non-ionic surfactant on the persistence of pesticides on/in fresh produce.

Another reason that this study is innovative is that it utilizes surface-enhanced Raman spectroscopy as a method for real-time, in situ pesticide detection. Pesticides are conventionally studied using methods such as gas chromatography and liquid chromatography (Yang et al., 2016; Huertas-Perez et al., 2023). However, these methods have various drawbacks that make them inefficient (Yang et al, 2016). Chromatography methods are time consuming and require qualified personnel to perform complicated extractions (Yang et al, 2016). Furthermore, chromatography is expensive, and many labs cannot afford the equipment (Yang et al, 2016). Lastly, and most importantly, chromatography does not allow for real-time, in situ, detection of pesticides (Yang et al, 2016). SERS, or surface-enhanced Raman spectroscopy has several advantages over traditional chromatography methods (Yang et al, 2016; Gracie et al., 2014; Wang et al., 2014; Zhou et al., 2014). SERS is fast, easy to use, and allows for real-time, in situ detection of pesticides with no destruction of the sample (Yang et al, 2016; Gracie et al., 2014; Wang et al., 2014; Zhou et al., 2014).

SERS is a combination of Raman spectroscopy and nanotechnology (Yang et al., 2016; Braun et al., 2009; Kneipp et al., 2006). Raman spectroscopy works by analyzing the scattering of photons when they interact with a sample (Du et al., 2023; Fan et al., 2014; Luo et al., 2014). When photons from the laser interact with the molecule of the sample, most of the photons scatter elastically, which is known as Raleigh scattering (Du et al., 2023; Fan et al., 2014; Luo et al., 2014). A few photons scatter inelastically, known as Raman scattering (Du et al., 2023; Fan et al., 2014; Luo et al., 2014). These inelastically scattered photons transfer some of their energy to the molecule, and as a result, lose energy and decrease in wavelength (Du et al., 2023; Fan et al., 2014; Luo et al., 2014). This decrease or Raman shift can be analyzed as every molecule produces a unique Raman spectrum based on the Raman shifts (Du et al., 2023; Fan et al., 2014; Luo et al., 2014). SERS also uses nanotechnology, in the form of nanoparticles such as gold or silver nanoparticles (Du et al., 2023; Fan et al., 2014; Luo et al., 2014). These nanoparticles act as hot spots and enhance the Raman signal of molecules that are otherwise difficult to detect (Du et al., 2023; Fan et al., 2014; Luo et al., 2014).

Thirdly, this study is innovative because it studies the use of baking soda and various starch granules to remove pesticide residues from fresh produce. It is both important and necessary to find a way for the public to clean their produce efficiently and effectively. Previous studies have found that using water by itself, as well as cleaning agents such as bleach, are not an effective method for removing pesticide residues (Yang et al., 2017). Using cheap and accessible household cleaners like baking soda and starch have shown promising results (Yang et al., 2017). This study aims to expand on these findings to by studying baking soda at different concentrations, and studying corn starch, rice starch, and flour to find the best method for removing pesticide residues. Starches such as corn starch, rice starch, and all-purpose flour can create Pickering emulsions and thus act as detergents (Chevalier et al., 2013; Mohammed 2022). Pickering emulsions occur when nanometer or micrometer particles absorb at the oil-water interface to create a physical barrier and reduce the interfacial energy (Chevalier et al., 2013). This is something that has not been studied with pesticides before and will help push the field forward.

Objectives

The overall goal of this study is to determine how a non-ionic surfactant affects pesticide behavior on the surface of fresh produce, and to find a common household material that can effectively remove >90% of pesticide residue in 5 minutes. to achieve this goal, there are 3 objectives:

1. Determine the impact of a non-ionic adjuvant on pesticide behaviors and SERS analysis on the surface of fresh produce.
    a. Determine the wetted area, evaporation rate, and SERS signals of Phosmet and Thiabendazole with and without Surf-Ac 910 on the surface of spinach and apple.
2. Determine the impact of adjuvants on the removal of pesticides from the surface off fresh produce using baking soda.

    a. Determine the removal efficacy of Thiabendazole with and without Surf-Ac 910 on the surface of an apple by a washing method (1% baking soda) at different time points.

3. Evaluate common household materials to reduce surface pesticide residues.

    a. Establish a home-practice approach in which Thiabendazole can be removed from the surface of an apple in 5 minutes or less. These methods include baking soda (1%, 2%, 5%, and 8%) and starch granules (cornstarch, rice starch, flour), and their combinations.

Chapter 2: Determine the impact of a non-ionic adjuvant on pesticide behaviors and SERS analysis on the surface of fresh produce.

Introduction

In real-world application of pesticides, pesticides are rarely applied as a pure chemical (Tu et al., 2023). Rather, pesticides are often combined with adjuvants designed to improve the functionality of the pesticide solution (Krogh et al., 2003; Kaczmarek et al., 2021; Wang et al., 2022). Adjuvants can improve various functions such as increasing the wetted area, increasing the evaporation rate, and improving the penetration (Du et al., 2023). Different adjuvants can have different effects and it is important to understand how these adjuvants change the behavior of pesticides since it directly effects how pesticide residues are removed.

Materials and Methods

Materials:

Thiabendazole (fungicide) and phosmet (insecticide) are of analytical reagent grade purchased from Sigma-Aldrich. Surf-Ac 910 (non-ionic surfactant) purchased from Drexel. Organic gala apples purchased from a local supermarket. Organic baby spinach purchased from a local supermarket. Citrate-capped AuNPs colloids purchased from NANO PARTZ Inc. Ultrapure water (18.2 MΩ cm) produced using Thermo Scientific Barnstead Smart2Pure Water Purification System and used for the preparation of solutions.

Methods:

Wetted Area:

To study the effects of a non-ionic surfactant on wetted area, two pesticides were chosen. The systemic pesticide that was chosen was thiabendazole. The non-systemic pesticide that was chosen was phosmet. For both pesticides, a concentration of 100 ppm was used. For application, 5 µL aliquots, at a concentration of 100 ppm, were pipetted onto the surface of either a washed and dried apple, or a washed and dried spinach leaf. 6 aliquots in total were applied, three of which were pure pesticide, and three of which were pesticide + adjuvant. Thiabendazole and phosmet were measured on different samples. For the solutions of pesticide + adjuvant, the concentration of Surf-Ac 910 was 0.25%. After application, the aliquots were imaged using a Jiusion 40 to 1000x USB microscope. One image was taken for each aliquot and the images were analyzed using the software AmScope.

Evaporation Rate:

To study the effects of a non-ionic surfactant on evaporation rate, two pesticides were chosen. The systemic pesticide that was chosen was thiabendazole. The non-systemic pesticide that was chosen was phosmet. For both pesticides, a concentration of 100 ppm was used. For application, 5 µL aliquots, at a concentration of 100 ppm, were pipetted onto the surface of either a washed and dried apple, or a washed and dried spinach leaf. 6 aliquots in total were applied, three of which were pure pesticide, and three of which were pesticide + adjuvant. Thiabendazole and phosmet were measured on different samples. For the solutions of pesticide + adjuvant, the concentration of Surf-Ac 910 was 0.25%. After application, a stopwatch was started immediately, and the evaporation rate was recorded once the aliquot had evaporated.

Surface Behaviors

To study the effects of a non-ionic surfactant on the surface behaviors of pesticides, two pesticides were chosen. The systemic pesticide that was chosen was thiabendazole. The non-systemic pesticide that was chosen was phosmet. For both pesticides, a concentration of 100 ppm was used. For application, 5 μL aliquots, at a concentration of 100 ppm, were pipetted onto either a washed and dried apple, or a washed and dried spinach leaf. 6 aliquots in total were applied, three of which were pure pesticide, and three of which were pesticide + adjuvant. For the solutions of pesticide + adjuvant, the concentration of Surf-Ac 910 was 0.25%. The aliquots were allowed to dry on the surface of the produce in a fume hood for different exposure times. The two exposure times that were tested were 40 minutes and 3 days. 40 min simulated short-term exposure and 3 days simulated long-term exposure. After exposure, a gold nanoparticle mirror was applied. The mirror was made by slowing adding 100 ml of mediating solvent to 50 ml of 250 ppm 50nm gold nanoparticle solution. The mediating solvent was made of a 1:1 mixture of hexanes and acetonitrile. When the mediating solvent was added to the gold, a mirror would aggregate at the bottom of the test tube. The top layer of liquid was removed, and the mirror was pipetted onto the surface of the apple where the pesticide was applied. 6 aliquots of gold mirror were applied in total, one for each aliquot of pesticide. The produce was then taken to the DXR Raman microscope for imaging. Furthermore, to prove the results where the result of the addition of Surf-Ac 910 and not the surface of the produce, the same experiment was performed on aluminum foil.

Penetration

To study systemic pesticides, 1000 ppm of thiabendazole was chosen as a model. To study non-systemic pesticides, 1000 ppm of phosmet was chosen as a model. 1000 ppm was chosen as the concentration to match the real-world application. For application, 5 µL aliquots, at a concentration of 1000 ppm, were pipetted onto the surface of a washed and dried apple. 6 aliquots in total were applied, three of which were pure pesticide, and three of which were pesticide + adjuvant. For the solutions of pesticide + adjuvant, the concentration of Surf-Ac 910 was 0.25%. The aliquots were allowed to dry on the surface of the apple in a fume hood for different exposure times. The two exposure times that were tested were 40 minutes and 3 days. 40 min simulated short-term exposure and 3 days simulated long-term exposure. After exposure, the apple was washed by submerging the apple in 200 ml of 1% baking soda solution for 27 minutes to remove any surface residues that could cause co-penetration. Previous research found 27 minutes to be long enough to remove 90% of surface residues. This was an important step since the gold nanoparticles can carry pesticide residues left on the surface into the tissue of the apple. The apple was blow dried after washing and a 5 µL aliquot of 250 ppm 50 nm gold nanoparticle solution was pipetted onto the surface of the apple where the pesticide was applied. 6 aliquots of gold nanoparticles were applied in total, one for each aliquot of pesticide. The gold nanoparticle aliquots were then allowed to dry in the fume hood for 40 minutes. Once dry, the apples were taken to the DXR Raman microscope for imaging.

Raman Instrumentation and Data Analysis:

A DXR Raman microscope (Thermo Fisher Scientific, Madison, WI) with a 780 nm laser and a 20× long distance microscope objective was used in this study. Each spectrum was scanned from 400 to 2000 cm^{-1} with 3 mW laser power and 2 s exposure time. For surface mapping, SERS images were obtained with a 50 µm slit aperture. Each mapping area was randomly selected with an area of 200 µm by 200 µm using a step size of 50 µm. For penetration depth mapping, a 50 µm pinhole aperture and a scanning depth of 300 µm was used. Each mapping area was randomly selected with one image containing 75 scanning spots. Raman mappings were analyzed using OMNIC software (Thermo Fisher Scientific).

Results

Wetted Area and Evaporation Rate:

The results of monitoring the effects of a non-ionic surfactant on the wetted area and evaporation rate of pesticides concluded that the addition of Surf-Ac 910 both increased the wetted area and the evaporation rate. There was no significant difference between thiabendazole and phosmet for both wetted area and evaporation rate, which suggests that whether the pesticide is systemic or non-systemic does not play a role in this experiment. Also, these results were consistent across both spinach and apple, suggesting that the type of produce does not play a role in this experiment.

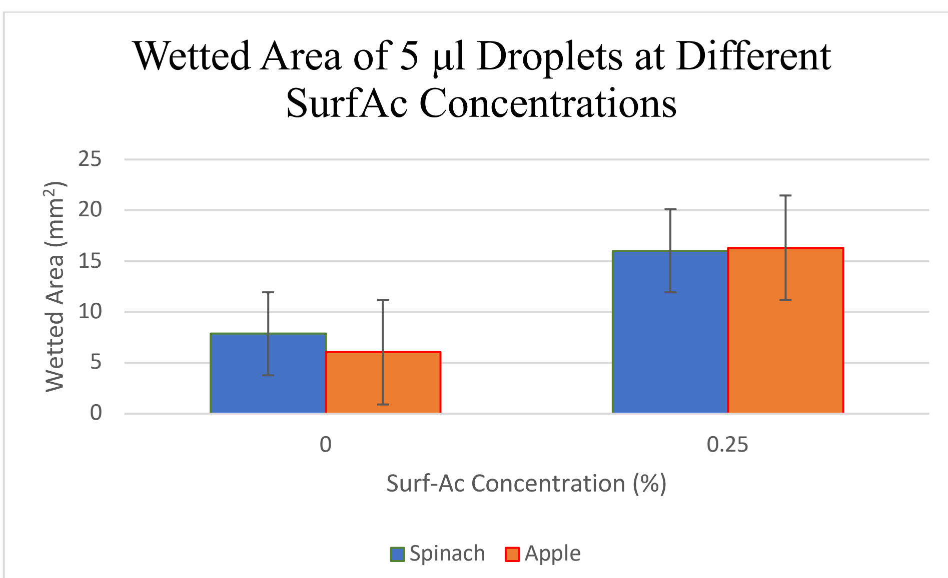

Figure 1: This figure compares the effects of Surf-Ac 910 on the wetted area for both spinach and apple surfaces. The left side of the graph has a Surf-Ac 910 concentration of 0, and the right side of the graph has a Surf-Ac 910 concentration of 0.25. The blue bars represent spinach, while the orange bars represent apple. The error bars were calculated using the standard deviation.

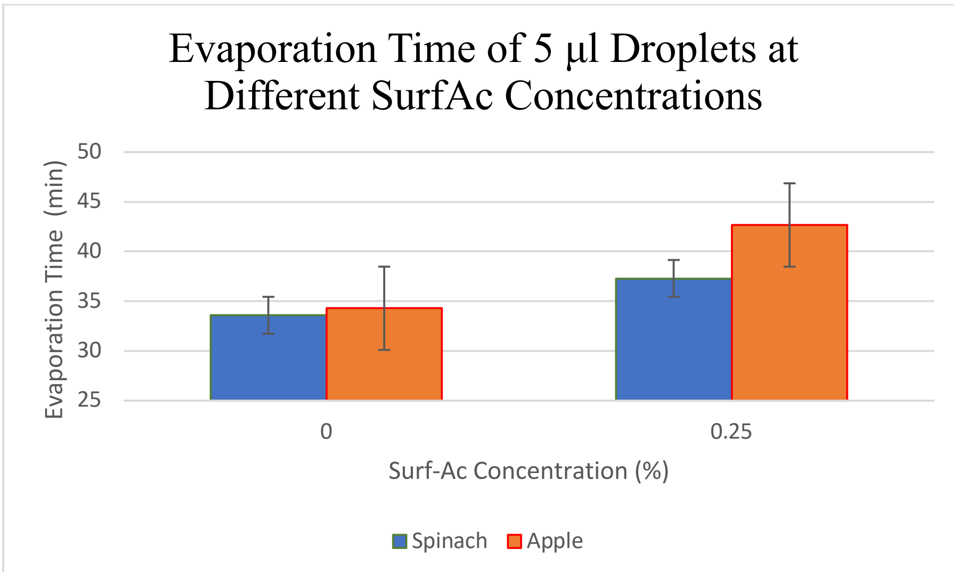

Figure 2: This figure compares the effects of Surf-Ac 910 on the evaporation time for both spinach and apple surfaces. The left side of the graph has a Surf-Ac 910 concentration of 0, and the right side of the graph has a Surf-Ac 910 concentration of 0.25. The blue bars represent spinach, while the orange bars represent apple. The error bars were calculated using the standard deviation.

Surface Behaviors:

The results of monitoring the effects of a non-ionic surfactant on the surface behaviors of pesticides suggest that the addition of Surf-Ac 910 decreased the Raman signal intensity of phosmet, while not significantly effecting thiabendazole. When looking at the Raman spectra for phosmet, the peak of interest is at 612 cm^{-1} which corresponds to C=O. When looking at the

Raman spectra for thiabendazole, the peaks of interest are at 785 cm^{-1} and 1014 cm^{-1} which correspond to C=N and C-N/C-C respectively.

Looking at pesticide exposure on spinach leaves, phosmet showed a large decrease in Raman intensity when Surf-Ac 910 was added to the pesticide solution. Phosmet on its own had an average Raman intensity of 643 at 612 cm^{-1}. Phosmet + Surf-Ac 910 had an average Raman intensity of 175 at 612 cm^{-1}. In contrast, thiabendazole did not show a significant change in Raman intensity when Surf-Ac 910 was added to the pesticide solution. Thiabendazole on its own had an average Raman intensity of 540 at 1014 cm^{-1}. Thiabendazole + Surf-Ac 910 had an average Raman intensity of 522 at 1014 cm^{-1}.

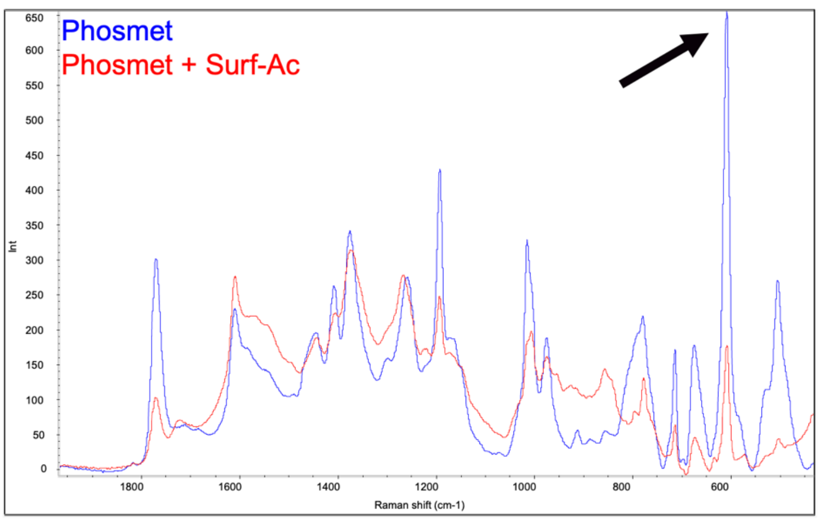

Figure 3: This figure shows the impact of Surf-Ac 910 on the surface Raman signal of phosmet while on a spinach leaf. The blue line represents pure phosmet, while the red line represents phosmet + Surf-Ac 910. The x-axis of the chart shows the Raman shift (cm^{-1}) and the y-axis shows the Raman intensity. The black arrow points to the peak of interest for phosmet, which is 600 cm^{-1}.

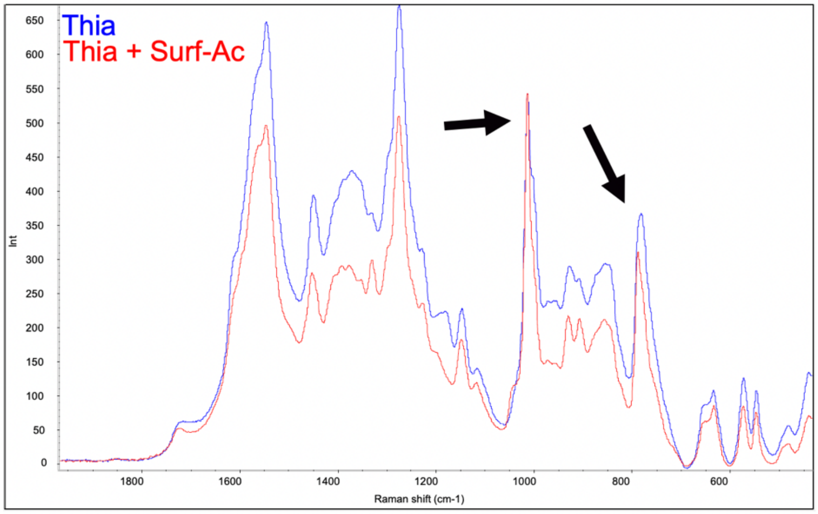

Figure 4: This figure shows the impact of Surf-Ac 910 on the surface Raman signal of thiabendazole while on a spinach leaf. The blue line represents pure thiabendazole, while the red line represents thiabendazole + Surf-Ac 910. The x-axis of the chart shows the Raman shift (cm^{-1}) and the y-axis shows the Raman intensity. The black arrow points to the peaks of interest for thiabendazole, which are 1014 cm^{-1} and 785 cm^{-1}.

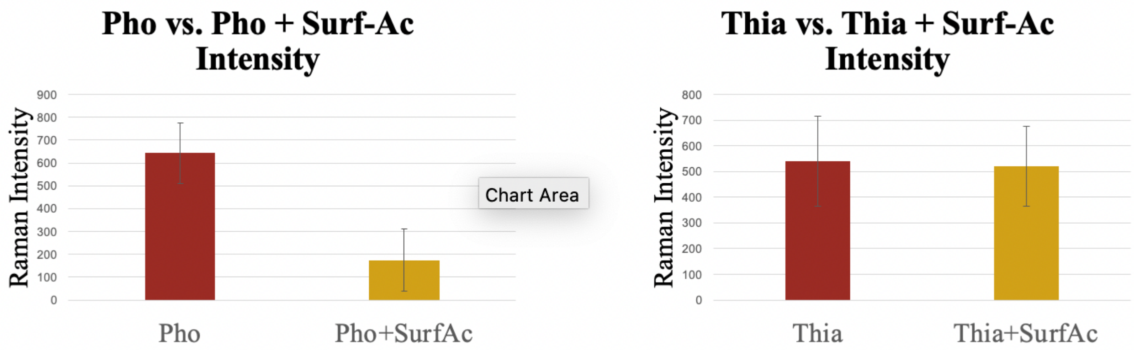

Figure 5: This figure shows the statistical significance of the Raman signal decrease for both phosmet and thiabendazole on spinach. The left side of the figure shows phosmet vs. phosmet + Surf-Ac 910. The right side of the figure shows thiabendazole vs. thiabendazole + Surf-Ac 910.

The y-axis shows the Raman intensity, and the error bars were calculated using the standard deviation.

Looking at pesticide exposure on the surface of an apple, phosmet showed a large decrease in Raman intensity when Surf-Ac 910 was added to the pesticide solution. Phosmet on its own had an average Raman intensity of 338 at 612 cm^{-1}. Phosmet + Surf-Ac 910 had an average Raman intensity of 22 at 612 cm^{-1}. In contrast, thiabendazole did not show a significant change in Raman intensity when Surf-Ac 910 was added to the pesticide solution. Thiabendazole on its own had an average Raman intensity of 478 at 1014 cm^{-1}. Thiabendazole + Surf-Ac 910 had an average Raman intensity of 427 at 1014 cm^{-1}.

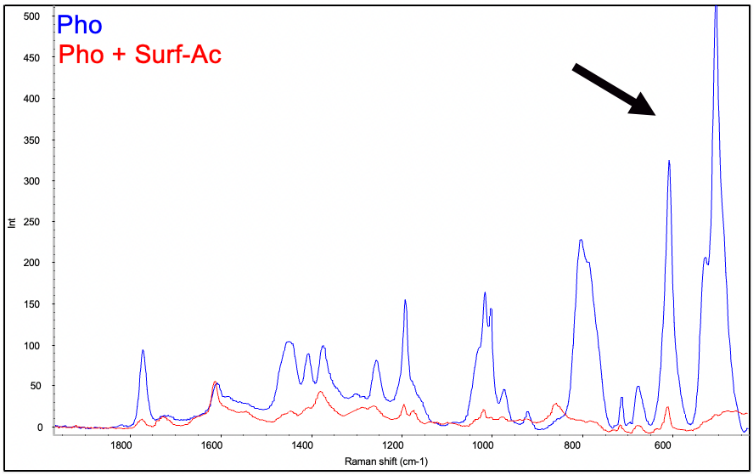

Figure 6: This figure shows the impact of Surf-Ac 910 on the surface Raman signal of phosmet while on an apple. The blue line represents pure phosmet, while the red line represents phosmet + Surf-Ac 910. The x-axis of the chart shows the Raman shift (cm^{-1}) and the y-axis shows the Raman intensity. The black arrow points to the peak of interest for phosmet, which is 600 cm^{-1}.

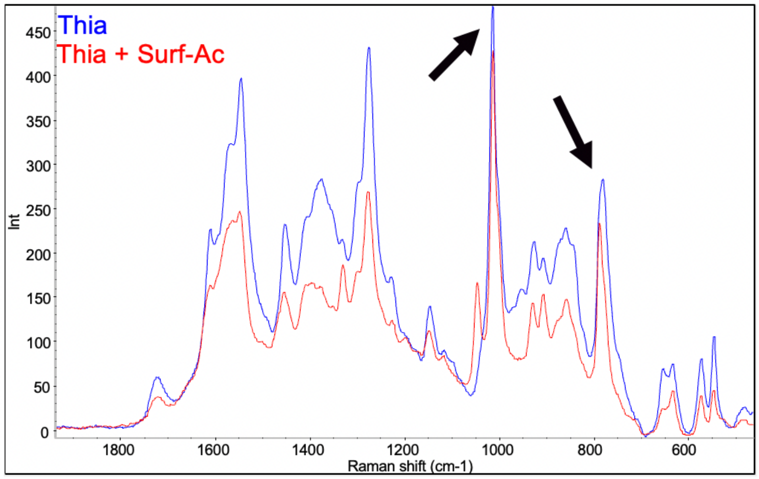

Figure 7: This figure shows the impact of Surf-Ac 910 on the surface Raman signal of thiabendazole while on an apple. The blue line represents pure thiabendazole, while the red line represents thiabendazole + Surf-Ac 910. The x-axis of the chart shows the Raman shift (cm^{-1}) and the y-axis shows the Raman intensity. The black arrow points to the peaks of interest for thiabendazole, which are 1014 cm^{-1} and 785 cm^{-1}.

The results for monitoring the surface behaviors of pesticides on aluminum foil showed that the Raman signal intensity for both phosmet and thiabendazole decreased significantly with the addition of Surf-Ac 910.

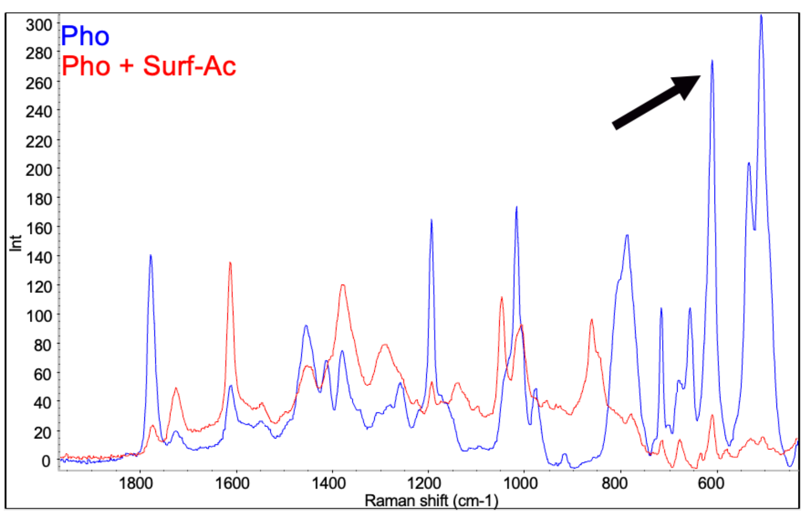

Figure 8: This figure shows the impact of Surf-Ac 910 on the surface Raman signal of phosmet while on aluminum foil. The blue line represents pure phosmet, while the red line represents phosmet + Surf-Ac 910. The x-axis of the chart shows the Raman shift (cm^{-1}) and the y-axis shows the Raman intensity. The black arrow points to the peak of interest for phosmet, which is 600 cm^{-1}.

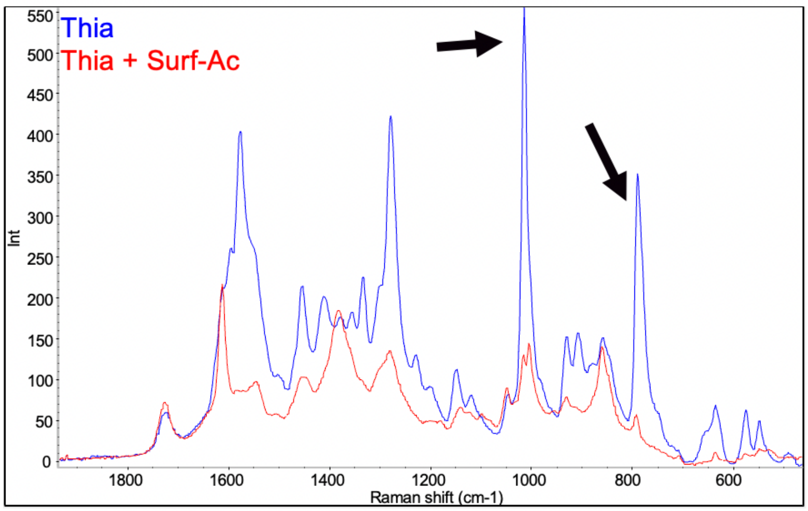

Figure 9: This figure shows the impact of Surf-Ac 910 on the surface Raman signal of thiabendazole while on aluminum foil. The blue line represents pure thiabendazole, while the red line represents thiabendazole + Surf-Ac 910. The x-axis of the chart shows the Raman shift (cm^{-1}) and the y-axis shows the Raman intensity. The black arrow points to the peaks of interest for thiabendazole, which are 1014 cm^{-1} and 785 cm^{-1}.

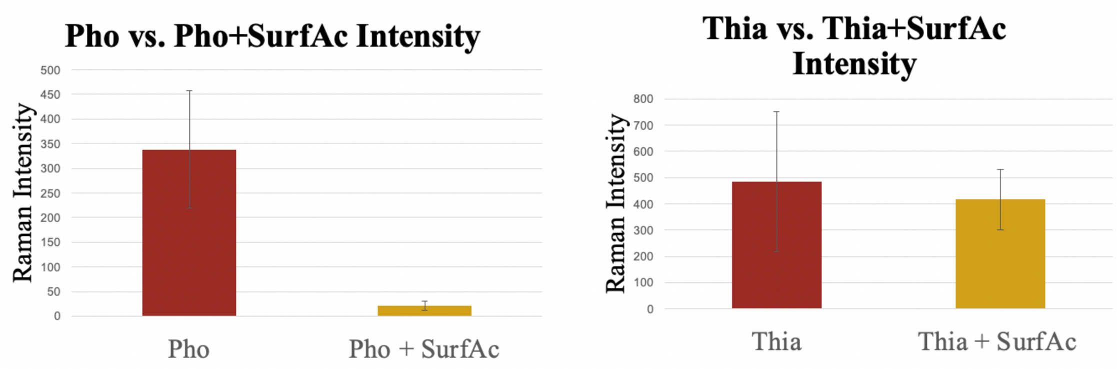

Figure 10: This figure shows the statistical significance of the Raman signal decrease for both phosmet and thiabendazole on apple. The left side of the figure shows phosmet vs. phosmet + Surf-Ac 910. The right side of the figure shows thiabendazole vs. thiabendazole + Surf-Ac 910. The y-axis shows the Raman intensity, and the error bars were calculated using the standard deviation.

Penetration:

The results of monitoring the penetration of thiabendazole into an apple, show that thiabendazole can successfully penetrate the apple tissue. Even as early as 40 min, the results show significant penetration to a depth of approximately 70-75 µm. This result was obtained through both looking at the depth mapping, and by analyzing the thiabendazole signal at different depths. When combined with the adjuvant, Surf-Ac 910, the penetration depth slightly increased. With increasing the exposure time to 3 days, the penetration does not significantly change for the thiabendazole group, but there is a greater increase on the thiabendazole + Surf-Ac 910 group.

The results of monitoring the penetration of phosmet into an apple, show that phosmet cannot successfully penetrate the apple tissue. Phosmet had a penetration depth of approximately 10-20 μm after 40 minutes of exposure. This result was obtained through both looking at the depth mapping and analyzing the phosmet signal at different depths. When combined with Surf-Ac 910, the penetration depth did not change. After 3 days of exposure, phosmet had the same penetration depth of about 10-20 μm.

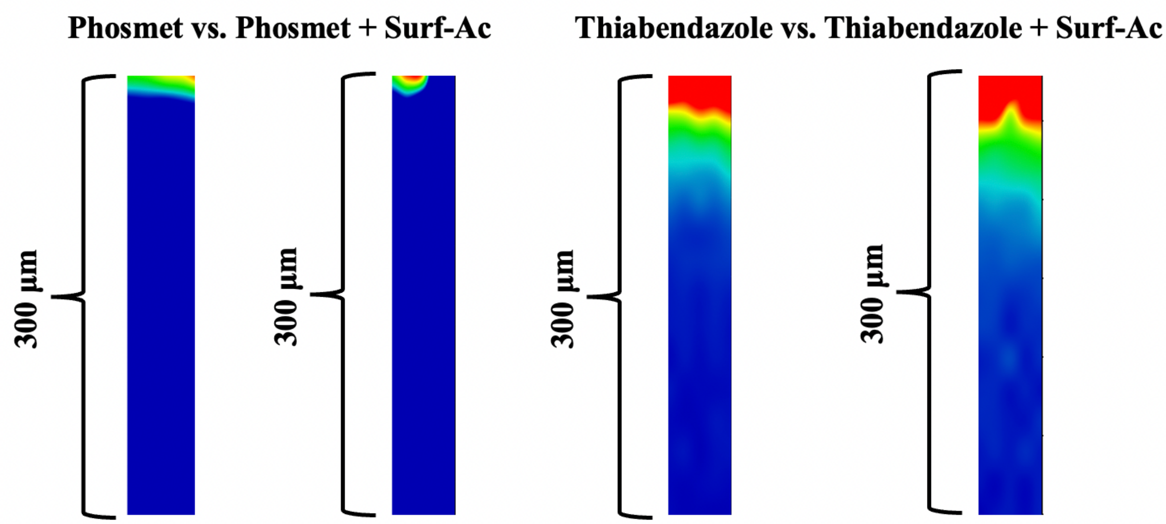

Figure 11: This figure shows the depth mapping for both phosmet and thiabendazole on apple after short-term exposure (40 minutes). The left side of the figure shows phosmet vs. phosmet + Surf-Ac 910. The right side of the figure shows thiabendazole vs. thiabendazole + Surf-Ac 910. The y-axis shows the depth from 0-300 um. Red color indicates a higher Raman signal, while blue color indicates a lower Raman signal.

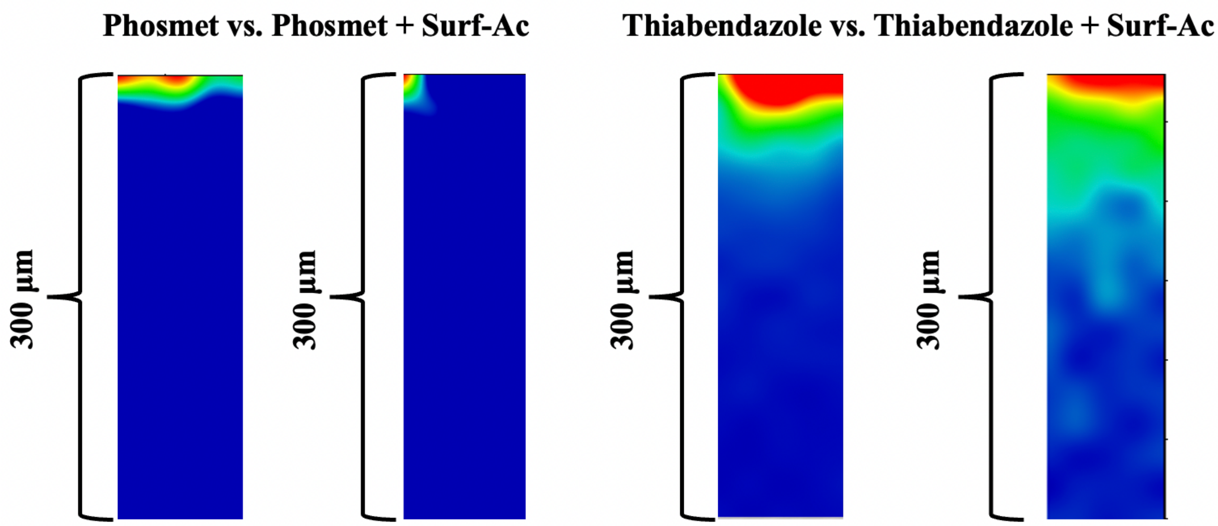

Figure 12: This figure shows the depth mapping for both phosmet and thiabendazole on apple after long-term exposure (40 minutes). The left side of the figure shows phosmet vs. phosmet + Surf-Ac 910. The right side of the figure shows thiabendazole vs. thiabendazole + Surf-Ac 910. The y-axis shows the depth from 0-300 um. Red color indicates a higher Raman signal, while blue color indicates a lower Raman signal.

Discussion

Understanding how adjuvants impact the behavior of pesticides and analytical method are crucial for establishing basic understanding of how pesticide formulations perform on fresh produce. In this chapter, four different experiments were performed to test the impact the adjuvants had on pesticide performance. The first experiment was the wetted area, and the results show that the addition of a non-ionic surfactant increased the maximum wetted area of both non-systemic and systemic pesticides. This increase was noted on both spinach and apple as well and was shown to be statically significant. This result is likely due to the non-ionic surfactant's ability to reduce the surface tension of the pesticide solution, and thus increasing the area of the droplet.

The second experiment was evaporation time, and the results show that the addition of a non-ionic surfactant increased the evaporation time of both non-systemic and systemic pesticides. This increase was noted on both spinach and apple as well and was shown to be statically significant. This result was expected, because adjuvants are used to maximize the time the active ingredient must absorb into the plant tissue.

The third experiment was studying the surface behaviors using SERS. For both apple and spinach, the results show that the addition of a non-ionic surfactant decreased the Raman signal intensity of phosmet, while not significantly effecting the Raman signal intensity of thiabendazole. However, when this experiment was repeated on aluminum foil to make sure the decrease in signal intensity was not due to the plant surface, it was found that there was a decrease in Raman signal intensity for both phosmet and thiabendazole when Surf-Ac 910 was added. This suggests that the reason phosmet has a decrease on produce, and not thiabendazole, is because of their behaviors as non-systemic and systemic pesticides respectively. Phosmet sits on the surface, and thus the Surf-Ac 910 can interact with the gold nanoparticles which inhibits phosmet's ability to interact with the gold nanoparticles. This results in no enhancement of phosmet's signal. On the other hand, thiabendazole can penetrate the produce tissue and thus Surf-Ac 910 is not interfering with the enhancement of the signal.

The fourth experiment was studying the penetration behaviors using SERS. Only apple was used for study. Thiabendazole was shown to successfully penetrate the apple tissue, while phosmet did not penetrate. This makes sense as thiabendazole is a systemic pesticide and phosmet is a non-systemic pesticide. The addition of Surf-Ac 910 slightly increased the penetration of thiabendazole, while not effecting the penetration of phosmet. This increase in penetration of the thiabendazole + Surf-Ac 910 group was more noticeable after long-term exposure (3 days). This is most likely the result of Surf-Ac 910's behavior as a non-ionic surfactant, which helps pesticide penetrate more effectively.

Chapter 3: Determine the impact of adjuvants on the removal efficacy of pesticides from apple surfaces using baking soda.

Introduction

The use of pesticides in agriculture is an effective way to protects crops and increase crop yield. However, pesticide residues can remain on produce post-harvest and then be consumed, potentially causing a health hazard (Food and Agriculture Organization of the United Nations, 2017; Savary et al., 2019). There has been increasing concern over the health effects of consuming pesticides, and as a result, there has been interest in how to best remove pesticide residues safely and effectively (Yang et al., 2017). Moreover, there is a push to use cleaning agents that are safe, easy to obtain, and more environmentally friendly (Yang et al., 2017). Household cleaning agents such as a baking soda are preferred to synthetic detergents for those reasons (Yang et al., 2017). The most common methods of household pesticide removal that have been studied include water, sodium chloride, sodium bicarbonate, and acetic acid (Yang et al., 2017). Previous studies have shown that compared to water, and even commercial detergents, baking soda is the most effective at removing surface pesticide residues (Yang et al., 2017). For this reason, 1% baking soda solution was chosen as the first washing method to be tested.

One piece of information that is missing from previous studies is the inclusion of adjuvants in the pesticide solution. The previous experiments done on the efficacy of baking soda for pesticide removal only looked at how well it removed pure pesticide compounds (Tu et al., 2023. This potentially leads to limited results as adjuvants could affect the removal of pesticides from the produce surface (Tu et al., 2023. For example, adjuvants could affect the non-systemic/systemic properties of pesticides and result in different penetration properties.

For this study the pesticide thiabendazole was chosen. Previous experiments done in this lab determined that thiabendazole is harder to remove from the surface of produce than phosmet, which has to do with its systemic properties. For this reason, thiabendazole is the focus of this chapter as any washing method that is effective for thiabendazole should be effective for phosmet as well. Phosmet will be tested again in a later chapter after the best washing method for thiabendazole removal is found. For the produce, apple was chosen. Apple was chosen because previous studies in this lab determined that it is harder to remove pesticide residues from the surface of an apple compared to spinach. Spinach will be tested again in a later chapter after the best washing method for apples is found.

Materials and Methods

Materials:

Thiabendazole (fungicide) is of analytical reagent grade purchased from Sigma-Aldrich. Surf-Ac 910 (non-ionic surfactant) purchased from Drexel. Organic gala apples purchased from a local supermarket. Baking soda purchased from local supermarket. Citrate-capped AuNPs colloids purchased from NANO PARTZ Inc. Ultrapure water (18.2 MΩ cm) produced using Thermo Scientific Barnstead Smart2Pure Water Purification System and used for the preparation of solutions.

Methods:

To study the effects of a non-ionic surfactant on the removal efficacy of pesticides using baking soda, thiabendazole was chosen as the pesticide. For thiabendazole, a concentration of 100 ppm was used. For application, 5 µL aliquots, at a concentration of 100 ppm, were pipetted onto a washed and dried apple. 6 aliquots in total were applied, three of which were pure pesticide, and three of which were pesticide + adjuvant. For the solutions of pesticide + adjuvant, the concentration of Surf-Ac 910 was 0.25%. The aliquots were allowed to dry on the surface of the produce in a fume hood for different exposure times. The two exposure times that were tested were 40 minutes and 3 days. 40 min simulated short-term exposure and 3 days simulated long-term exposure. After exposure, the apples were submerged in 200 ml of 1% baking soda solution for different times. The washing time was increased until 90% of the pesticide surface signal was removed. The washed apples were then rinsed with water and dried. The section of apple where the pesticide was applied was cut off and put in a dish for the gold nanoparticle mirror application. The mirror was made by slowing adding 100 ml of mediating solvent to 50 ml of 250 ppm 50nm gold nanoparticle solution. The mediating solvent was made of a 1:1 mixture of hexanes and acetonitrile. When the mediating solvent was added to the gold, a mirror would aggregate at the bottom of the test tube. The top layer of liquid was removed, and the mirror was pipetted onto the surface of the apple where the pesticide was applied. 6 aliquots of gold mirror were applied in total, one for each aliquot of pesticide. The produce was then taken to the DXR Raman microscope for imaging.

Edit to Methods:

After the experiment was performed, the concentration of thiabendazole was increased from 100 ppm to 1000 ppm. This was due to there not being a Raman signal for the thiabendazole + Surf-Ac 910 group after long-term exposure. 1000 ppm is also closer to the real-world application concentration, and it allows for the decrease in Raman signal intensity during washing to be more easily observed.

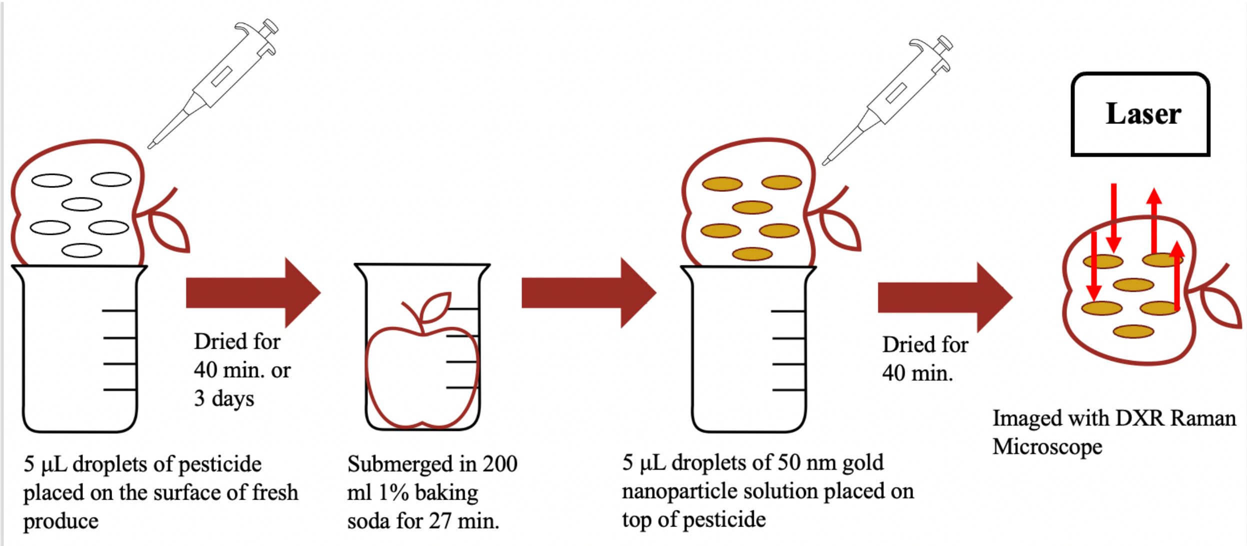

Figure 13: This figure depicts the baking soda washing method described above.

Raman Instrumentation and Data Analysis:

A DXR Raman microscope (Thermo Fisher Scientific, Madison, WI) with a 780 nm laser and a 20× long distance microscope objective was used in this study. Each spectrum was scanned from 400 to 2000 cm^{-1} with 3 mW laser power and 2 s exposure time. For surface mapping, SERS images were obtained with a 50 μm slit aperture. Each mapping area was randomly selected with an area of 200 μm by 200 μm using a step size of 50 μm. Raman mappings were analyzed using OMNIC software (Thermo Fisher Scientific).

<u>Results</u>

Thiabendazole vs. Thiabendazole + Surf-Ac 910 – Short-term Exposure:

The results of monitoring the effects of a non-ionic surfactant on the efficacy of 1% baking soda as a removal method for pesticide residues after short-term exposure, concluded that the addition of Surf-Ac 910 did not significantly affect the removal time. For both thiabendazole and thiabendazole + Surf-Ac 910 groups, there was a 90% decrease in the Raman signal intensity after 27 minutes. This suggests that for short term pesticide exposure, 27 minutes of washing with 1% baking soda solution is enough to remove pesticide residues from the surface of produce with or without and adjuvant present. The only difference between the two pesticide groups is that after 5 min of washing with the 1% baking soda solution, the thiabendazole + Surf-Ac 910 group has a more significant decrease in Raman signal intensity than the thiabendazole group. This decrease does not change the overall removal time but is important to note.

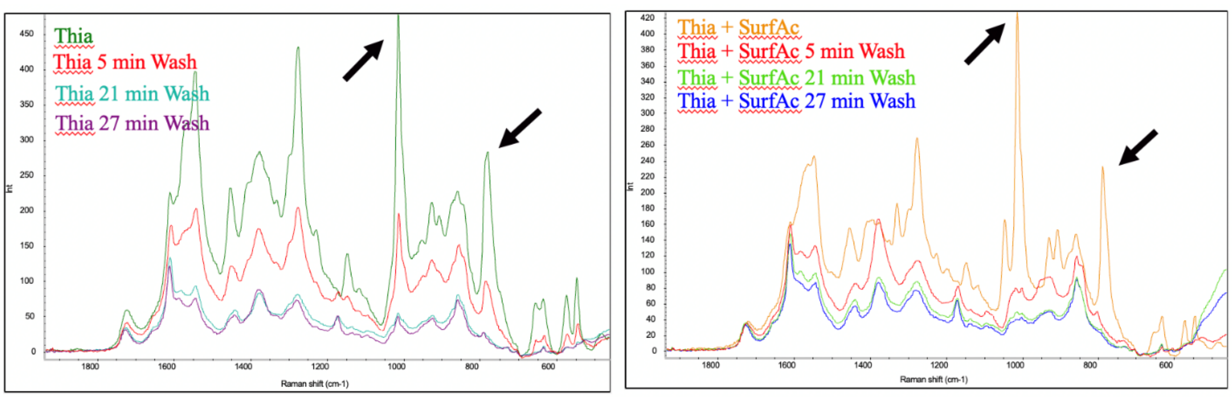

Figure 14: This figure compares the Raman spectra for thiabendazole and thiabendazole + SurfAc-910 after short-term exposure and 1% baking soda wash. The panel on the left shows the Raman spectra for pure thiabendazole at different washing times using 1% baking soda solution. The panel on the right shows the Raman spectra for thiabendazole + Surf-Ac 910 at different washing times using 1% baking soda solution. The black arrows point to the peaks of interest of thiabendazole at 1014 cm^{-1} and 785 cm^{-1}.

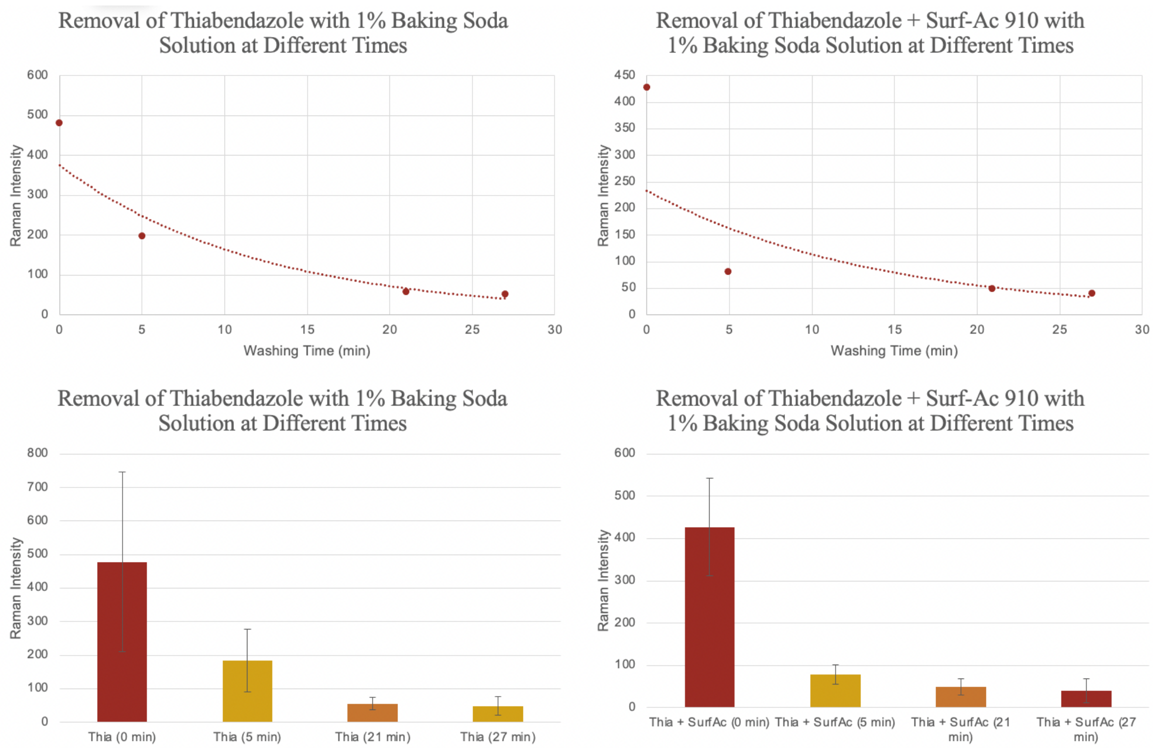

Figure 15: This figure shows the efficacy of 1% baking soda solution for removing thiabendazole and thiabendazole + Surf-Ac 910 after short-term exposure. The upper left panel shows the curve for the removal of pure thiabendazole using 1% baking soda solution. This line graph corresponds to the bar graph in the bottom left panel. The upper right panel shows the curve for the removal of thiabendazole + Surf-Ac 910 using 1% baking soda solution. This line graph corresponds to the bar graph in the bottom right panel. The error bars were calculated using the standard deviation.

Thiabendazole vs. Thiabendazole + Surf-Ac 910 – Long-term Exposure:

The results of monitoring the effects of a non-ionic surfactant on the efficacy of 1% baking soda as a removal method for pesticide residues after long-term exposure, concluded that the addition of Surf-Ac 910 showed an increase in Raman signal intensity during an increase in washing time. For pure thiabendazole, there was a 75% decrease in Raman signal intensity after 27 minutes of washing with 1% baking soda solution. This suggests that compared to the short-term exposure, after long-term exposure the pesticide residue is harder to remove from the surface of the produce. For thiabendazole + Surf-Ac 910, the data was inconsistent with the patterns previously noticed in the short-term exposure group. Instead of the increase in washing time resulting in a decrease in Raman signal intensity, the increase in washing time appeared to result in an increase in Raman signal intensity. This result gave the appearance that the amount of pesticide residue on the surface of the apple was increasing, which does not make sense. We speculated that this is due to the penetration of the pesticides in deeper areas, so that when the surface layer was removed, more pesticides that penetrated in deeper areas were exposed. To combat this problem, the concentration was raised from 100 ppm to 1000 ppm. 1000 ppm is closer to the real-world concentration that is applied to produce, and it allows for more surface residues to be analyzed for surface removal capability of 1% baking soda.

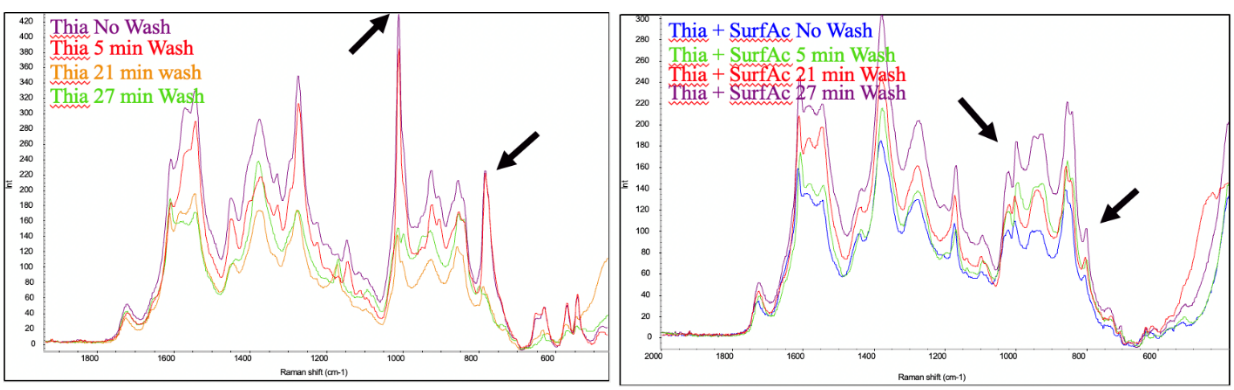

Figure 16: This figure compares the Raman spectra for thiabendazole and thiabendazole + SurfAc-910 after long-term exposure and 1% baking soda wash. The panel on the left shows the Raman spectra for pure thiabendazole at different washing times using 1% baking soda solution. The panel on the right shows the Raman spectra for thiabendazole + Surf-Ac 910 at different

washing times using 1% baking soda solution. The black arrows point to the peaks of interest of thiabendazole at 1014 cm^{-1} and 785 cm^{-1}.

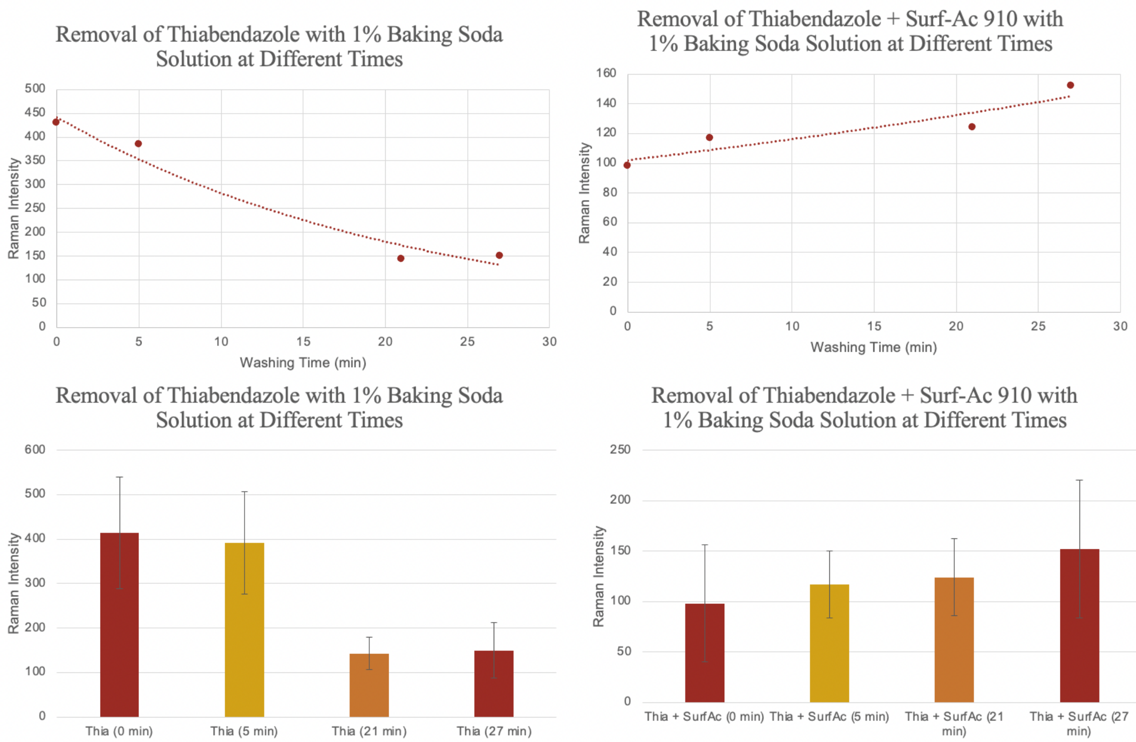

Figure 17: This figure shows the efficacy of 1% baking soda solution for removing thiabendazole and thiabendazole + Surf-Ac 910 after long-term exposure. The upper left panel shows the curve for the removal of pure thiabendazole using 1% baking soda solution. This line graph corresponds to the bar graph in the bottom left panel. The upper right panel shows the curve for the removal of thiabendazole + Surf-Ac 910 using 1% baking soda solution. This line graph corresponds to the bar graph in the bottom right panel. The error bars were calculated using the standard deviation.

Thiabendazole 100 ppm vs. 1000 ppm:

The results of monitoring the effects of a non-ionic surfactant on the efficacy of 1% baking soda as a removal method for pesticide residues using 1000 ppm instead of 100 ppm, concluded that 1000 ppm does fix the previous problem of not seeing a Raman signal for the pesticide.

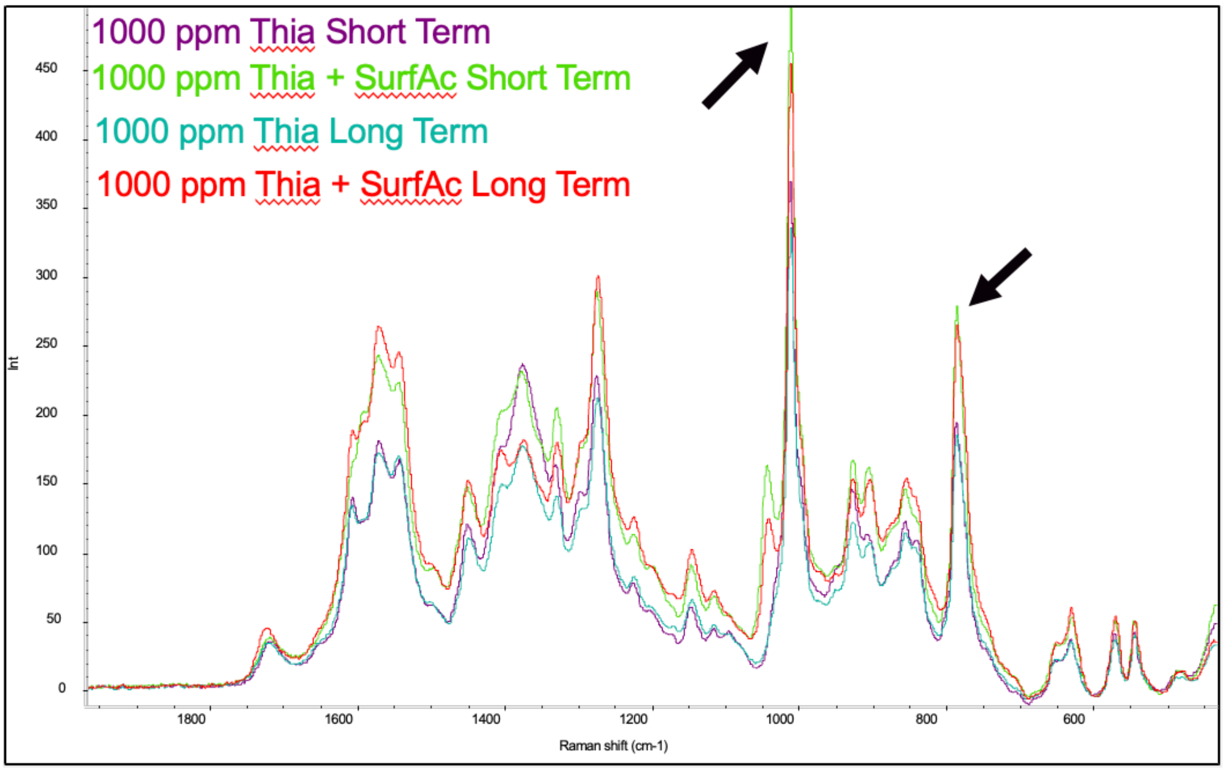

Figure 18: This figure compares the Raman spectra for thiabendazole and thiabendazole + Surf-Ac 910 after the concentration was increased to 1000 ppm. The black arrows point to the peaks of interest of thiabendazole at 1014 cm^{-1} and 785 cm^{-1}.

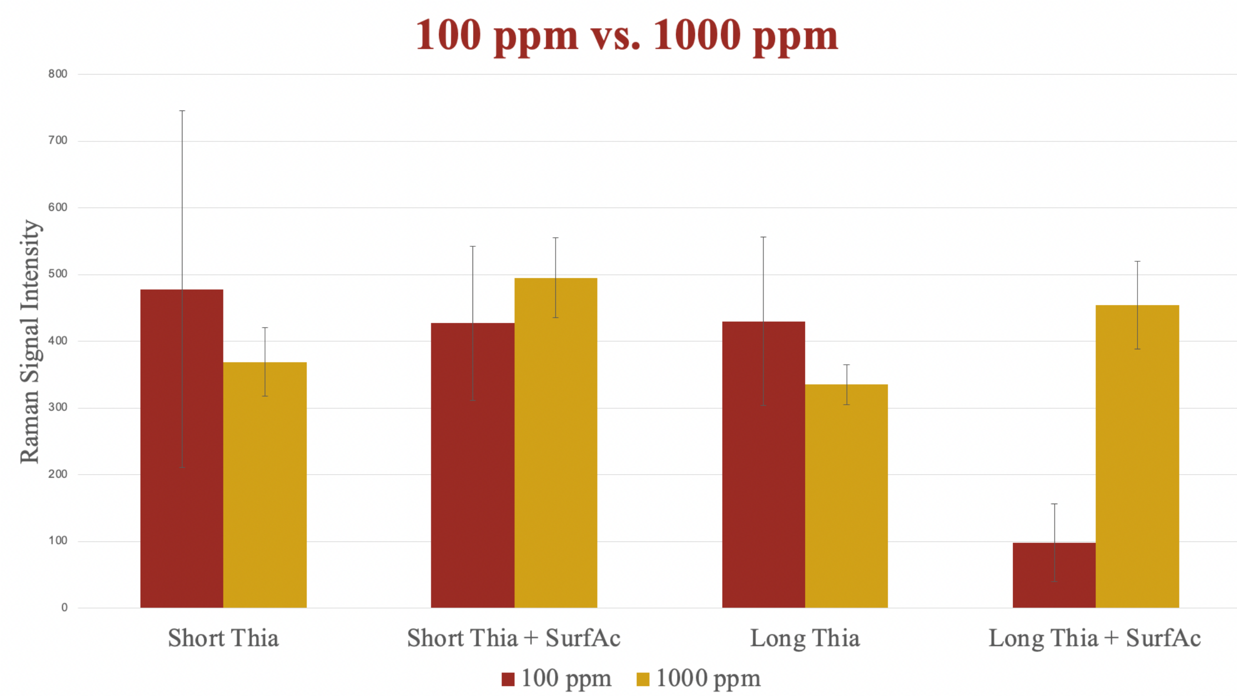

Figure 19: This figure compares the Raman signal intensity of 100 ppm and 1000 ppm for both thiabendazole and thiabendazole + Surf-Ac 910. The red bars represent 100 ppm, and the yellow bars represent 1000 ppm. The error bars were calculated using the standard deviation.

Discussion

In this chapter, the impact of a non-ionic surfactant on the efficacy of 1% baking soda as a removal method for pesticide residues was tested. A systemic pesticide, thiabendazole with and without Surf-Ac 910, was applied to the surface of an apple for either 40 minutes or 3 days. 40 minutes simulated short-term exposure, and 3 days simulated long-term exposure. The results show that after 40 minutes of exposure, there is no significant impact that Surf-Ac 910 has on the removal efficacy of 1% baking soda. The 1% baking soda solution was able to remove 90% of the pesticide residues for both groups in 27 minutes. The results show that after 3 days of exposure, there is a significant difference when Surf-Ac 910 is added. The pure thiabendazole group had a similar pattern to that of the short-term exposure, but with less of a decrease in Raman signal intensity after 27 minutes. Only 75% of the pesticide residue was able to be removed after 27 minutes of washing in 1% baking soda solution. This suggests that an increase in exposure time makes the pesticide residues more difficult to remove. The thiabendazole + Surf-Ac 910 group already had a very low Raman signal for thiabendazole at 0 min washing. It is possible that this low signal could be the result of Surf-Ac 910 aiding the thiabendazole in penetrating into the apple tissue. To increase the Raman signal for this group and better visualize the effects of washing, the concentration of thiabendazole was increased from 100 ppm to a 1000 ppm. After making this change, the thiabendazole + Surf-Ac 910 had a Raman signal and showed a similar trend to pure thiabendazole. Overall, Surf-Ac 910 did not appear to impact the efficacy of 1% baking soda, but the exposure time did have an impact. The long-term exposure group had a much higher Raman signal for thiabendazole after 27 minutes of washing compared to the short-term exposure group.

Chapter 4: Evaluate common household materials to reduce surface pesticide residues.

Introduction

There has been an increasing desire to find alternatives to synthetic detergents used to remove pesticide residues from the surface of produce (Yang et al., 2017). Previous studies have shown that household materials, such as baking soda, are effective at removing surface pesticide residues (Yang et al., 2017). Exploring more household materials as a means for reducing pesticide residues is desirable since the public has easy access to these materials. For instance, starches are abundant, inexpensive, and sustainable. Starch granules can also act as effective detergents due to the formation of Pickering emulsions. (Chevalier et al., 2013; Mohammed 2022). Pickering emulsions are made with nanometer or micrometer particles that adsorb at the oil-water interface (Chevalier et al., 2013; Mohammed 2022). The particles form a physical barrier around the oil droplet and reduce the interfacial energy, allowing for easy removal (Chevalier et al., 2013; Mohammed 2022). This adsorption is almost irreversible and starch granules can form Pickering emulsions with a variety of compounds, including pesticides (Chevalier et al., 2013; Mohammed 2022).

Materials and Methods

Materials:

Thiabendazole (fungicide) is of analytical reagent grade purchased from Sigma-Aldrich. Surf-Ac 910 (non-ionic surfactant) purchased from Drexel. Organic gala apples purchased from a local supermarket. Baking soda purchased from local supermarket. Corn starch ordered online. Rice starch ordered online. All-purpose flour ordered online. Citrate-capped AuNPs colloids purchased from NANO PARTZ Inc. Ultrapure water (18.2 MΩ cm) produced using Thermo Scientific Barnstead Smart2Pure Water Purification System and used for the preparation of solutions.

Methods:

To study and compare the efficacy of different pesticide removal methods, thiabendazole was chosen as the pesticide. For thiabendazole, a concentration of 1000 ppm was used. For application, 5 µL aliquots, at a concentration of 1000 ppm, were pipetted onto a washed and dried apple. 6 aliquots in total were applied, three of which were pure pesticide, and three of which were pesticide + adjuvant. For the solutions of pesticide + adjuvant, the concentration of Surf-Ac 910 was 0.25%. The aliquots were allowed to dry on the surface of the produce in a fume hood for different exposure times. The exposure times that were tested were 40 minutes and 3 days. 40 min simulated short-term exposure and 3 days simulated long-term exposure. For the removal method, several different solutions were tested. These included 5% baking soda, 8% baking soda, 1% corn starch, 1% rice starch, and 1% all-purpose flour. The most effective baking soda concentration and most effective starch granule were combined and tested as well. While testing different concentrations of baking soda, both 40 minutes and 3 days of exposure were tested. While testing different starch granules, only 40 minutes was tested. After exposure, the apples were submerged in 200 ml of washing solution for 5 minutes. The washed apples were then rinsed with water and dried. The section of apple where the pesticide was applied was cut off and put in a dish for the gold nanoparticle mirror application. The mirror was made by slowing adding 100 ml of mediating solvent to 50 ml of 250 ppm 50nm gold nanoparticle solution. The mediating solvent was made of a 1:1 mixture of hexanes and acetonitrile. When the mediating solvent was added to the gold, a mirror would aggregate at the bottom of the test tube. The top layer of liquid was removed, and the mirror was pipetted onto the surface of the apple where the pesticide was applied. 6 aliquots of gold mirror were applied in total, one for each aliquot of pesticide. The produce was then taken to the DXR Raman microscope for imaging.

Edit to Methods:

After the experiment was performed, 2% concentrations of all the starch granules were added to the methods. Another member of the lab discovered that increasing the concentration of the starch granules from 1% to 2% made a significant difference. 2% baking soda was also included as a control.

Furthermore, it was suspected that the pesticide solution being used was less than 1000 ppm. A new pesticide solution was made for testing the starch granules and this new solution was used to repeat data for 1% baking soda and 2% baking soda.

Results

Different Concentrations of Baking Soda:

The results of comparing different concentrations of baking soda as a method of pesticide removal show that with an increase in baking soda concentration there is an increase in surface Raman signal intensity. This trend is notable in both 40 minute and 3-day exposure, and this trend is statistically significant. 1% baking soda appears to be the most effective baking soda concentration at removing surface pesticide residues, while 5% and 8% show an increase in surface Raman signal intensity.

While looking at the efficacy of different baking soda concentrations after 40 minutes of exposure, the concentration with the lowest Raman signal intensity after washing is 1% baking soda. The Raman signal intensity after washing with 1% baking soda is 184 (117 stdv) for pure thiabendazole, and 239 (87 stdv) for thiabendazole + Surf-Ac 910. Increasing the baking soda concentration to 5% increased the Raman signal intensity after washing to 395 (142 stdv) for pure thiabendazole and 298 (100 stdv) for thiabendazole + Surf-Ac 910. For 8% baking soda, the Raman signal intensity after washing is 440 (68 stdv) for pure thiabendazole and 264 (53 stdv) for thiabendazole + Surf-Ac 910.

While looking at the efficacy for different concentrations after 3 days of exposure, the concentration with the lowest Raman signal intensity after washing is also 1% baking soda. The Raman signal intensity after washing with 1% baking soda is 93 (30 stdv) for pure thiabendazole, and 194 (91 stdv) for thiabendazole + Surf-Ac 910. Increasing the baking soda concentration to 5% increased the Raman signal intensity after washing to 362 (77 stdv) for pure thiabendazole and 385 (60 stdv) for thiabendazole + Surf-Ac 910. For 8% the Raman signal intensity after washing is 335 (47 stdv) for pure thiabendazole and 545 (45 stdv) for thiabendazole + Surf-Ac 910.

After the experimental data was collected, it was suspected that the 1000 ppm thiabendazole solution being used was incorrectly made. The solution appeared to be less than 1000 ppm, and so a new thiabendazole solution was made. The data for 1% baking soda was recollected, and 2% baking soda was added into the methods. The Raman signal intensity after washing with 1% baking soda is 449 (95 stdv) for pure thiabendazole and 407 (93 stdv) for thiabendazole + Surf-Ac 910. The Raman signal intensity after washing with 2% baking soda is 440 (103 stdv) for pure thiabendazole and 336 (85 stdv) for thiabendazole + Surf-Ac 910.

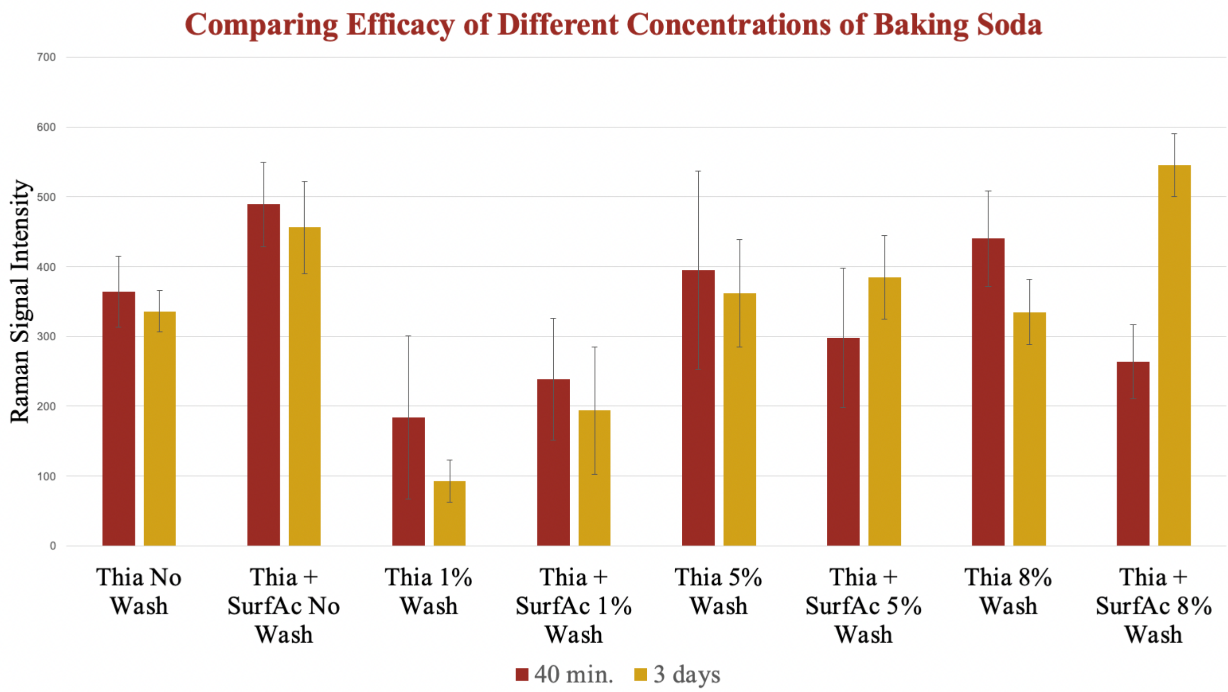

Figure 20: This figure shows the comparison in efficacy of different concentration of baking soda for removing thiabendazole and thiabendazole + Surf-Ac 910 after both short and long-term exposure. The bars represent the surface Raman signal intensity after either no wash or washing with 1%, 5%, or 8% baking soda. The red bars represent the surface Raman signal intensity after 40 minutes of exposure. The yellow bars represent the surface Raman signal intensity after 3 days of exposure. For each group tested (No wash, 1% baking soda, 5% baking soda, and 8% baking soda) there is set of bars for both pure thiabendazole and thiabendazole + Surf-Ac 910. The error bars were calculated using the standard deviation.

Starch Granules:

The results of comparing different types of starch granules as a method of pesticide removal show that 2% corn starch appears to be the most effective at removing surface pesticide residues. 2% corn starch shows the largest decrease in Raman signal intensity compared to the not washed control apples. This is true for both the pure thiabendazole group and for thiabendazole + Surf-Ac 910.

First, 1% concentrations of the starch granules were tested. The Raman signal intensity after washing with 1% corn starch is 496 (93 stdv) for pure thiabendazole, and 438 (74 stdv) for thiabendazole + Surf-Ac 910. The Raman signal intensity after washing with 1% rice starch is 500 (54 stdv) for pure thiabendazole and 430 (93 stdv) for thiabendazole + Surf-Ac 910. The Raman signal intensity after washing with 1% flour is 334 (41 stdv) for pure thiabendazole and 190 (43 stdv) for thiabendazole + Surf-Ac 910.

2% concentrations of the starch granules were tested after another member of the lab found that they are significantly more effective than 1% starch solutions. The Raman signal intensity after washing with 2% corn starch is 268 (83 stdv) for pure thiabendazole, and 150 (47 stdv) for thiabendazole + Surf-Ac 910. The Raman signal intensity after washing with 2% rice starch is 384 (68 stdv) for pure thiabendazole and 340 (62 stdv) for thiabendazole + Surf-Ac 910. The Raman signal intensity after washing with 2% flour is 260 (45 stdv) for pure thiabendazole and 209 (67 stdv) for thiabendazole + Surf-Ac 910.

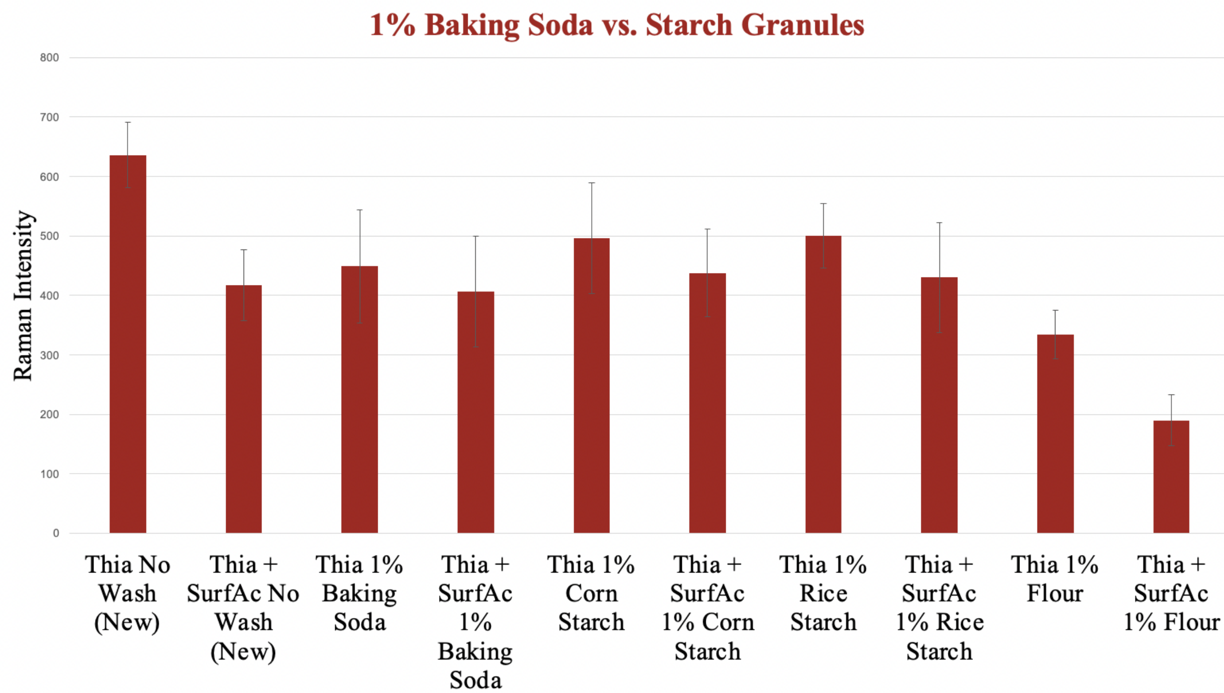

Figure 21: This figure shows the comparison in efficacy between 1% baking soda and different starch granules for removing thiabendazole and thiabendazole + Surf-Ac 910 after short-term exposure. The bars represent the surface Raman signal intensity after either no wash or washing with 1% baking soda, corn starch, rice starch, or all-purpose flour. For each group tested, there is a bar for both pure thiabendazole and thiabendazole + Surf-Ac 910. For this graph the new solution of 1000 ppm thiabendazole was used, and this is denoted as Thia No Wash (New) and Thia + SurfAc No Wash (New). The error bars were calculated using the standard deviation.

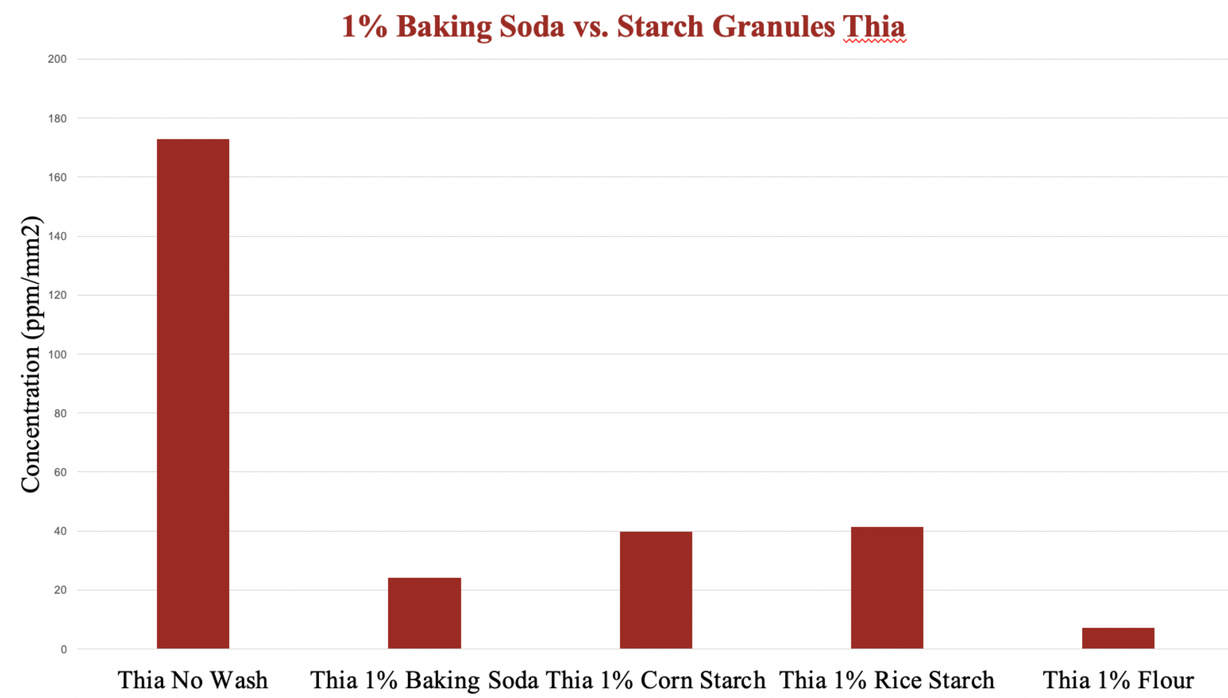

Figure 22: This figure shows the comparison in efficacy between 1% baking soda and different starch granules for removing thiabendazole after short-term exposure. The bars represent the surface concentration after either no wash or washing with 1% baking soda, corn starch, rice starch, or all-purpose flour. The concentration values were calculated using a standard curve for thiabendazole. For this graph the new solution of 1000 ppm thiabendazole was used, and this is denoted as Thia No Wash. The error bars were calculated using the standard deviation.

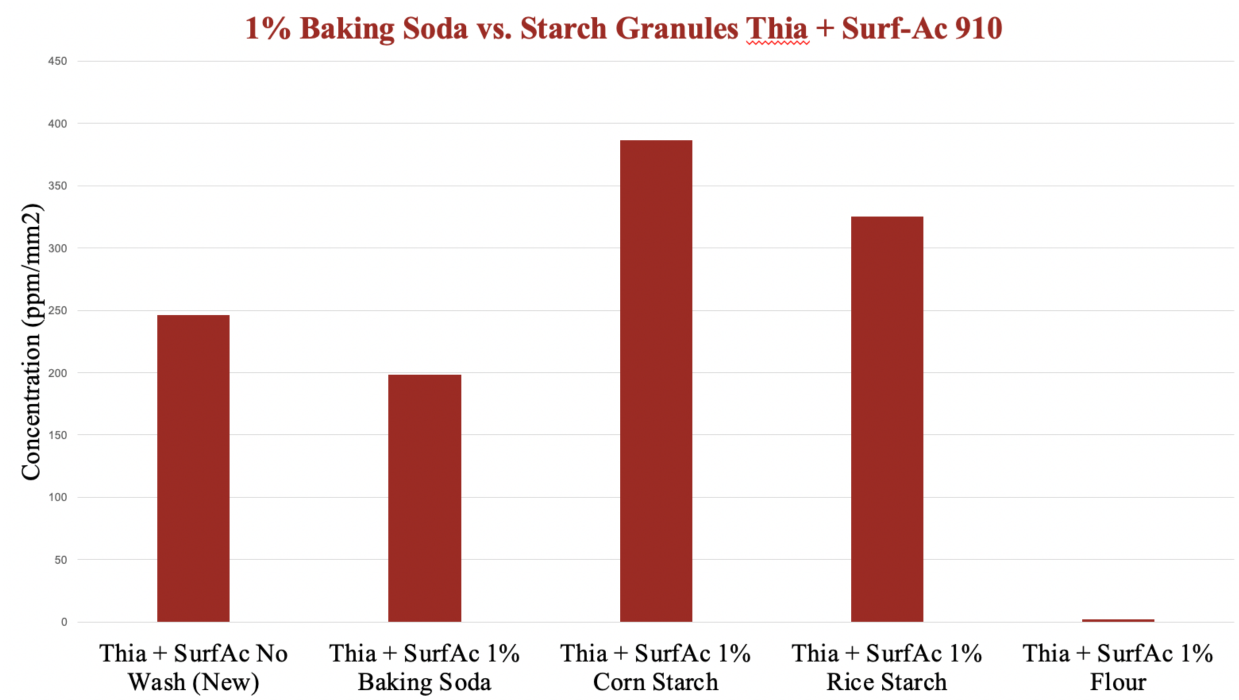

Figure 23: This figure shows the comparison in efficacy between 1% baking soda and different starch granules for removing thiabendazole + Surf-Ac 910 after short-term exposure. The bars represent the surface concentration after either no wash or washing with 1% baking soda, corn starch, rice starch, or all-purpose flour. The concentration values were calculated using a standard curve for thiabendazole + Surf-Ac 910. For this graph the new solution of 1000 ppm thiabendazole was used, and this is denoted as Thia + SurfAc No Wash (New). The error bars were calculated using the standard deviation.

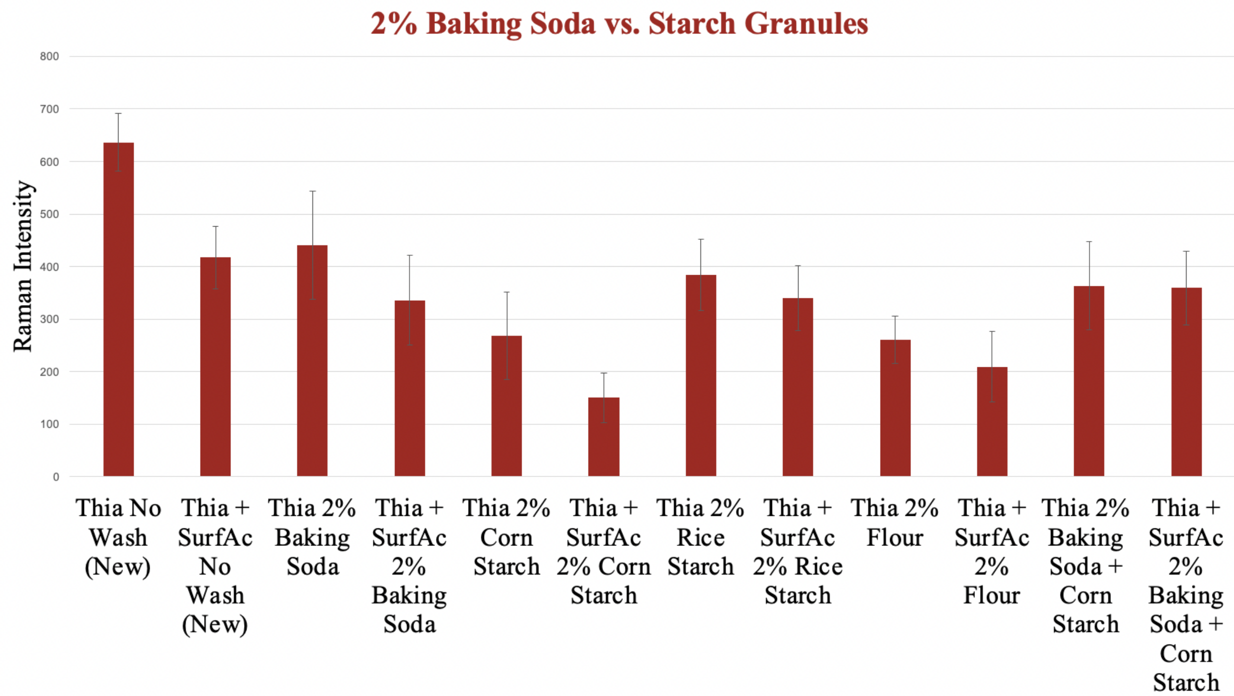

Figure 24: This figure shows the comparison in efficacy between 2% baking soda and different starch granules for removing thiabendazole after short-term exposure. The bars represent the surface Raman signal intensity after either no wash or washing with 2% baking soda, corn starch, rice starch, or all-purpose flour. For this graph the new solution of 1000 ppm thiabendazole was used, and this is denoted as Thia No Wash (New) and Thia + SurfAc No Wash (New). The error bars were calculated using the standard deviation.

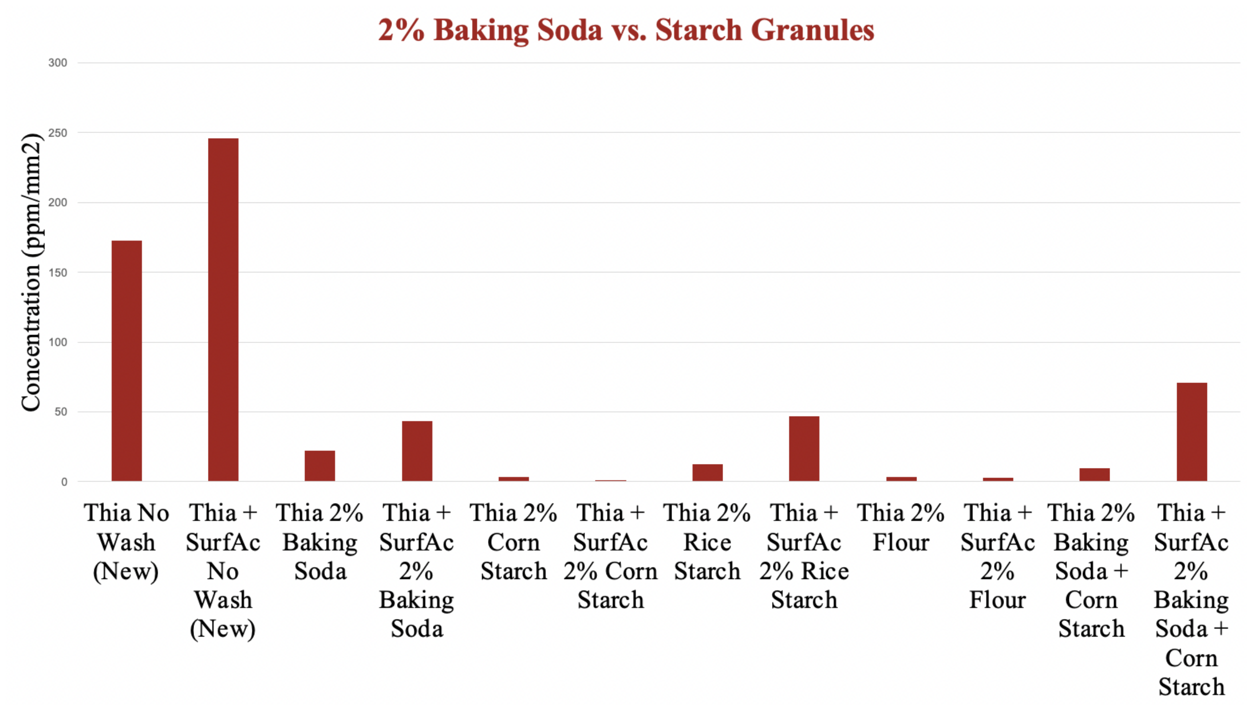

Figure 25: This figure shows the comparison in efficacy between 2% baking soda and different starch granules for removing thiabendazole after short-term exposure. The bars represent the surface concentration after either no wash or washing with 2% baking soda, corn starch, rice starch, or all-purpose flour. The concentration values were calculated using a standard curve for thiabendazole. For this graph the new solution of 1000 ppm thiabendazole was used, and this is denoted as Thia No Wash (New) and Thia + SurfAc No Wash (New). The error bars were calculated using the standard deviation.

Combination of Baking Soda and Corn Starch:

The results of taking the most effective baking soda concentration and combining it with the most effective starch granule showed an increase in surface Raman signal intensity compared to starch by itself. For the baking soda, a concentration of 2% was used. For the starch granule, 2% corn starch was used. The surface Raman signal intensity after washing with this combination is 363 (84 stdv) for thiabendazole and 359 (70 stdv) for thiabendazole + Surf-Ac 910. This is compared to 2% corn starch having a surface Raman signal intensity after washing of 268 (83 stdv) for thiabendazole and 150 (47 stdv) for thiabendazole + Surf-Ac 910

Discussion

In this chapter, the impact of a non-ionic surfactant on the efficacy of various washing methods for pesticide residues was tested. Different concentrations of baking soda, corn starch, rice starch, and all-purpose flour were tested. A systemic pesticide, thiabendazole with and without Surf-Ac 910, was applied to the surface of an apple for either 40 minutes or 3 days. 40 minutes simulated short-term exposure, and 3 days simulated long-term exposure. The results show that after both 40 minutes and 3 days of exposure, there was a significant decrease in the removal efficacy baking soda when increasing the baking soda concentration. This pattern was present for both thiabendazole with and without Surf-Ac 910 and was most likely due to the alkali hydrolysis of baking soda. A higher concentration of baking soda could lead to greater degradation of the outer wax layer of the apple. This degradation could expose pesticide residues that had penetrated the tissue of the produce, and thus cause the surface Raman signal intensity to be higher, as we discussed in the previous chapter, although 1000 ppm pesticide concentration was applied. If this is true, then the net pesticide residues for 5% and 8% are lower than 1% and 2%. More experiments (e.g. testing at different time points) are needed to test this assumption.

The results for the different starch granules show that there was a significant difference between 1% and 2% starch solutions. Starch granules are effective detergents because they can form Pickering emulsions that adsorb at the oil-water interface and provide a physical barrier of solid particles around the oil droplet, allowing for easy removal (Chevalier et al., 2013; Mohammed 2022). Increasing the starch concentration to 2% seemed to make these Pickering emulsions significantly more effective. Overall, 2% corn starch was the most effective when looking at both thiabendazole and thiabendazole + Surf-Ac 910. After only 5 minutes of washing with 2% corn starch, 98% of thiabendazole residues and over 99% of thiabendazole + Surf-Ac 910 residues were removed from the surface of the apple. 2% flour was also very effective, removing around 98% of both thiabendazole and thiabendazole + Surf-Ac 910 residues. Being over 90% effective in only 5 minutes makes these methods viable options for use in real world applications.

Additionally, a combination of 2% baking soda and 2% corn starch was tested and the results show that it was less effective at removing pesticide residues than 2% corn starch alone. The combination solution has a surface Raman signal intensity after washing of 363 (84 stdv) for thiabendazole and 359 (70 stdv) for thiabendazole + Surf-Ac 910. This is compared to 2% corn starch having a surface Raman signal intensity after washing of 268 (83 stdv) for thiabendazole and 150 (47 stdv) for thiabendazole + Surf-Ac 910. The combination being less effective could be the result of the baking soda interfering with the formation of Pickering emulsions, which make the corn starch less effective as a removal method. This idea is supported by the fact that the combination solution has a similar surface Raman signal intensity to the 2% baking soda, implying that the baking soda is working but not the starch. More experiments are needed to verify this.

Chapter 5: Conclusion and Future Studies

Conclusion

In conclusion, the impact of a non-ionic surfactant on pesticide persistence in/on fresh produce was studied. For both phosmet, a non-systemic pesticide, and thiabendazole, a systemic pesticide, the addition of Surf-Ac 910 increased the maximum wetted area and evaporation time. This is due to Surf-Ac 910 reducing the surface tension of the pesticide droplets.

When looking at the surface behaviors of pesticide using surface-enhanced Raman spectroscopy, Surf-Ac 910 decreased the Raman signal intensity of phosmet. However, Surf-Ac 910 did not affect the Raman signal intensity of thiabendazole. This is due to phosmet's nature as a non-systemic pesticide. Phosmet does not penetrate the produce tissue, and therefore the Surf-Ac 910 sitting on the surface is interacting with the gold nanoparticle mirror and preventing phosmet's Raman signal from being enhanced.

Surf-Ac 910 was shown to aid thiabendazole's penetration into the tissue of apples. The addition of Surf-Ac 910 showed an increase in penetration depth of thiabendazole, but no difference in phosmet. This makes sense since phosmet does not have penetration behavior. Moreover, longer exposure made the pesticide residues harder to be removed from the surface of produce. This in combination with Surf-Ac 910 decreasing the surface Raman signal intensity after 3-day exposure supports the idea that Surf-Ac 910 helps pesticides penetrate produce.

1% and 2% baking soda were the most effective baking soda concentrations at removing pesticide residues. There was no statistically significant difference between 1% and 2% but increasing the concentration to 5% and 8% shows an increase in surface Raman signal intensity. This was mostly likely due to higher concentrations of baking soda breaking down the wax layer of the apple and exposing penetrated pesticide residues. This needs to be tested in further experiments. In terms of starch granules, 2% corn starch was the most effect starch granule at removing surface pesticide residues. A combination of corn starch and baking soda was tested as well, though it was shown to be less effective than corn starch alone. This could be due to the baking soda interfering with the formation of Pickering emulsions. More experiments are needed to confirm this.

Future Studies

In addition to the experiments that are needed to test the relationship between baking soda concentration and removal efficacy and the combination method, there are several other studies that should be conducted to further the understanding of how adjuvants effect pesticide persistence. Using the methods described in this study, there are several other materials that should be tested. For one, thiabendazole and phosmet were explored in this study, but there are a multitude of other pesticides to test. It is important to make sure that the findings of this study remain true for different types of pesticides and their active ingredients. This is also true for different types of adjuvants. Besides non-ionic surfactants, there are oils and acidifiers/buffers that have varying properties and could lead to different results. Another material of this study that should be changed is the type of produce. Different surfaces of different types of produce could affect the results and change the behaviors of pesticide.

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