Measuring exposure to strobilurin fungicides in strawberries, grapes, and spinach: Does washing the produce make a difference?

By

Stella Wang

Dr. Heather Stapleton, Advisor

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Executive Summary

Consumption of foods containing pesticide residues is one of the major pathways by which people are exposed to pesticides. Fungicides are an important class of pesticides, and previous research indicates that not only are certain fungicide application rates increasing, but also fungicide residues on produce can be relatively high on some produce, such as berries, leading to potential health concerns. Attention to strobilurin fungicides, a relatively new class of fungicides, in particular has been growing due to their widespread application, potential toxic effects on metabolic processes, and concerns that exposure may be a risk factor for neurodegenerative diseases. This study aimed to quantify potential exposure to four strobilurins (azoxystrobin, fluoxastrobin, pyraclostrobin, and trifloxystrobin) and to determine whether fungicide residues on certain produce items were considered a health risk. Furthermore, this research sought to determine if different washing techniques could reduce exposure and, therefore, risk. Exposure was evaluated by purchasing organic and generic varieties of grapes, strawberries, and spinach from three local grocery stores in Durham, North Carolina. The effect of two different produce washing treatments was evaluated by comparing residue concentrations on produce samples that were either rinsed with cold tap water or washed with a commercial produce detergent. Results demonstrate that pyraclostrobin and trifloxystrobin were the most commonly detected of the four strobilurin compounds monitored. Organic varieties had residue levels that were below the method detection limit. On average, residue levels were 18.07 ng/g pyraclostrobin and 15.01 ng/g trifloxystrobin on generic strawberries, and 19.6 ng/g pyraclostrobin and 0.4 ng/g trifloxystrobin on generic grapes. None of the four strobilurin fungicides were detected above trace levels in the spinach samples tested. For strawberries, tap washing removed approximately 52% of trifloxystrobin residue and the Ecos produce detergent removed 45%; for grapes, tap washing removed 72% of pyraclostrobin residue and the Ecos produce detergent removed 83%. Using the maximum amount detected in this study, exposure estimates were calculated for an average adult and child and compared with the acute and chronic reference doses. Overall, hazard quotients were less than one, indicating that exposure to fungicides from consumption of these items is less than the reference doses established by the US EPA, suggesting minimal to no risk.

Introduction

Strobilurins are a relatively new class of fungicide compounds that are emerging as environmental contaminants of concern. They are derived from natural fungicidal products from the myxothiazol bacterium *Myxococcus fulvus* and small fungi found on decaying wood (Roberts et al. 2007). Since first being synthesized and distributed in 1996, strobilurin fungicide use has been on the rise as they can be applied to a wide range of crops including cereals, grapevines, fruit, and vegetables. As early as 1999, the chemical class made up over 10% of the global market of fungicides (Bartlett et al. 2002). In 2012 alone, over 1 million kg of azoxystrobin, 0.1 million kg of fluoxastrobin, 2 million kg of pyraclostrobin, and 0.5 million kg of trifloxystrobin were applied in the US (Pearson et al. 2016; Luz et al. 2018).

Strobilurin compounds act by inhibiting the quinone outside (Qo) site of cytochrome bc_1 of mitochondrial complex III. This inhibits electron transfer between the cytochrome b and c complexes, ultimately disrupting the production of ATP (Bartlett et al. 2002; Pearson et al. 2016). These pesticides are classified as low risk to birds, mammals, bees, and humans, which greatly contributes to their growing popularity (Bartlett et al. 2002). For example, the strobilurin compound pyraclostrobin is not considered a concern for reproductive susceptibility, mutagenicity, genotoxicity, immunotoxicity, and carcinogenicity in humans (US Environmental Protection Agency 2013). Research suggests that this low toxicity to non-target organisms is due to their more rapid toxicokinetics relative to fungi (Balba 2007; Roberts et al. 2007).

Strobilurin compounds are also notable for their relatively short persistence in the environment. US EPA models predict that the biodegradation half-life in soil for azoxystrobin, the world's biggest-selling fungicide, is 4.3 days (Chemistry Dashboard n.d.; Balba 2007). However, some studies have shown conflicting results. One study found that azoxystrobin had a half-life of 56-84 days and 14 days in laboratory and field soils, respectively (Balba 2007; US Environmental Protection Agency 2013). Another laboratory-controlled experiment estimated that its half-life ranged from 15.1 to 25.8 days in brackish water (Gustafsson et al. 2010).

This variability in half-lives is concerning, and presents a challenge for predicting exposure to strobilurins, and therefore their potential impact on ecological and human health. Limited studies on humans exist, and one using human lymphocytes suggests that, at high enough doses, pyraclostrobin may induce genotoxicity and cytotoxicity (Çayır, Coskun, and Coskun 2014; US Environmental Protection Agency 2013). Another research study that used murine pre-adipocyte cell cultures indicates that pyraclostrobin induces mitochondrial dysfunction and increases triglyceride accumulation *in vitro*; it therefore raises questions about whether exposure could be a risk factor for metabolic syndromes (e.g. cardiovascular disease, type II diabetes, obesity) (Luz et al. 2018). Just as important are observations in cell cultures that demonstrate that many strobilurin compounds transcriptionally mimic autism spectrum

disease, neurodegeneration (Alzheimer's disease and Huntington's disease), and brain aging (Pearson et al. 2016). These results imply that exposure may present a risk to human health. In contrast, US EPA rodent acute and subchronic assays implied negligible risk (US Environmental Protection Agency 2013; Pearson et al. 2016).

Studies of strobilurin compounds' effects on other organisms may provide additional insight, especially regarding effects from chronic exposure. For example, the lowest observed effect concentrations (LOEC) of pyraclostrobin and trifloxystrobin that elicited reproductive effects in *Daphnia magna* were 0.15 μg/L and 0.2 μg/L, respectively, both of which are close to environmental concentrations (Cui et al. 2017). In wetlands and streams, a concentration of 1.7 μg/L of pyraclostrobin is considered environmentally-relevant and may have a sublethal effect on time to metamorphosis for tadpoles (Hartman et al. 2014).

Current human exposure data for strobilurin fungicides is lacking and leads to uncertain exposure estimates. A risk assessment on chronic and acute effects of pesticide exposure via consumption of apples indicates that fungicides make up the most frequently detected class of pesticides, and interestingly, multiple types of fungicides are usually present (Lozowicka 2015). However, such studies are lacking in data for strobilurins. Some, including pyraclostrobin, are not monitored in the environment and have very little data on potential human exposure available, creating significant uncertainty in exposure estimates. Biomonitoring data is also difficult to obtain due to the compounds' rapid metabolism in people; not only are multiple metabolites created, but many are also too unstable to serve as reliable biomarkers of exposure. Regardless, human exposure is likely since pyraclostrobin has been detected at levels ranging from 4 to 20 ppm on produce products, with particularly high concentrations on leafy green vegetables (Pearson et al. 2016). It is unclear whether chronic exposure to these fungicides via the diet may be enough to elicit sublethal health effects and changes in mitochondrial function and neurodevelopmental deficits.

Limiting dietary exposure can be a way to reduce overall exposure. Studies have shown that washing strawberries with ozonated water (Lozowicka et al. 2016), blanching spinach (Bonnechère et al. 2012), and submerging grapes in tap water can be effective strategies in decreasing pesticide residues on food products (Lentza-Rizos, Avramides, and Kokkinaki 2006). However, these studies were field experiments in which pesticide application was controlled and crops were immediately processed upon harvesting. This, along with the fact that such produce processing techniques as ozone washing are impractical for most people, makes it unlikely that these results represent the true exposure that typical consumers face.

Granted, some studies do attempt to simulate consumer exposure to pesticides by testing produce bought from local grocers and more typical produce washing techniques; they conclude that rinsing

produce reduces pesticide residues (Krol et al. 2000; Kruve et al. 2007; Michaels et al. 2003). These studies are relatively outdated, though, as they do not include this new class of strobilurin fungicides. Based on their rather high octanol-water partition coefficient values (log K_{ow}), these fungicides may not be readily washed off produce surfaces with water.

Predicting the level of pesticide residues on produce using computer models may be a solution when field or research data is lacking, but current literature shows that these approaches are not so simple or always accurate. Models rely on the physicochemical properties of chemicals; when washing produce with water, these properties do not always accurately predict residue removal. Furthermore, researchers disagree on how much we should rely on these predictors. Krol et al. suggest that the water solubility of pesticides is not a significant factor in predicting their removal from food crops, whereas Lozowicka et al. posit that the aqueous solubility and log K_{ow} values are the key factors. Other aspects such as how plants store pesticides or the composition of the produce's surface wax also influence pesticide residue levels at the point of purchase (Krol et al. 2000; Lozowicka et al. 2016, 1; López-Fernández, Rial-Otero, and Simal-Gándara 2013; Guardia-Rubio, Ayora-Cañada, and Ruiz-Medina 2007). Therefore, it may be difficult to predict the amount of residue removed by washing produce with water. For example, assuming that the water solubility and the octanol-water partition coefficient are the best predictors of removal by tap water washing, it would be expected that trifloxystrobin and pyraclostrobin would have the lowest percent removal, when comparing tap washed and unwashed samples, because they have the lowest water solubility and highest log K_{ow} values (Table 1).

Table 1. Key physicochemical properties of select strobilurin fungicide compounds (EPA Chemistry Dashboard).

Compound	Log K_{ow} (octanol-water)	Water Solubility (mol/L)	Vapor Pressure (mmHg)	Log K_{oa} (octanol-air)
Azoxystrobin	2.84	1.26e-5	2.95e-11	11.7
Fluoxastrobin	3.52	4.39e-6	5.69e-9	11.7
Pyraclostrobin	4.08	6.69e-5	5.77e-9	11.7
Trifloxystrobin	4.91	4.56e-6	3.15e-6	9.58

If fungicide residues are present on store-bought produce, it is important to understand how washing may affect potential exposure. While consuming organic produce varieties, which have fewer pesticide residues than their generic, non-organic counterparts, can reduce pesticide exposure, they have a notable economic cost for consumers (Winter and Davis 2006; Baker et al. 2002; Pearson et al. 2016). The 10-40% price premium on organic produce correlates with decreased willingness to pay for organic

varieties despite consumers' knowledge of risks of consuming pesticides (Winter and Davis 2006; Williams and Hammitt 2001; Gil, Gracia, and Sánchez 2000). Socioeconomic status and purchasing power are consequently influential factors in consumer purchasing behavior in which lower income correlates with decreased willingness to pay for organic produce (Ward et al. 2013; Neff et al. 2009; Yue and Tong 2009; Curl et al. 2013). This is significant when considering a recent EPA finding that food levels of pyraclostrobin, for example, can exceed toxic doses (Pearson et al. 2016; Lozowicka et al. 2016). Therefore, for consumers either unwilling or unable to purchase organic varieties, the ability to properly wash the cheaper generic variety prior to consumption is vital to minimizing pesticide exposure.

This study had three main objectives. The first was to estimate the potential exposure of consumers to the strobilurin fungicides azoxystrobin, fluoxastrobin, pyraclostrobin, and trifloxystrobin on organic and generic strawberries, grapes, and spinach. These produce types were selected based on their high pesticide residue scores and known application of specific strobilurin compounds (Environmental Working Group 2018; "Pesticide Data Program - Annual Summary, Calendar Year 2015" 2016). This study also sought to assess the efficacy of different consumer produce washing techniques, namely rinsing generic produce with cold tap water and specially marketed produce detergent, that may affect the amount of fungicide residue present prior to consumption. Finally, this study estimated the health risk of this exposure by calculating hazard quotients using the measured fungicide levels on the produce and comparing the exposure estimate to reference doses found in the literature.

Methods

SAMPLE COLLECTION AND PREPARATION

Generic and organic varieties of strawberries, grapes, and spinach were purchased from three different grocery stores in Durham, North Carolina (Stores A, B, and C) in September 2019. Generic varieties of each produce were then split and treated three ways: unwashed, washed with cold tap water for 30 s, or treated with the produce detergent Ecos according to application instructions. After treatment, each sample was then further processed as described below.

To prepare generic strawberries samples, one 16 oz shell container was divided into approximately three equal groups, with about seven strawberries (leaves and stems removed) per group. The unwashed group of berries was directly homogenized. Homogenization was accomplished by placing samples into a glass bowl from a Black & Decker Food Chopper and pulsing until the produce was ground into small pea-sized chunks. The tap wash treatment group was placed into a stainless-steel colander, rinsed with cold tap water for 30 s, air dried for 2 min, and then homogenized as described above. The Ecos group was treated according to product instructions: berries were placed into a colander,

sprayed 10 times with the Ecos produce detergent, let sit for 2 min, and wiped off with a paper towel before homogenizing. To prepare the sample containing organic strawberries, approximately seven berries were selected from a 16 oz container and homogenized.

Generic grape samples were prepared using the same process. From one bag of generic red table grapes, groups of approximately 32 grapes each were selected and washed according to treatment. To prepare the sample of organic grapes, 32 grapes were homogenized from a bag of organic red table grapes.

To process generic spinach samples, one bunch of spinach was divided into three approximately equal sized groups. Stems were cut manually with scissors. Leaves were then either directly homogenized (no wash group); rinsed under cold tap water for 30 s, air dried for 2 min, and homogenized (tap wash group); or washed with Ecos produce detergent according to product instructions for leafy greens. For the Ecos treatment, spinach leaves were placed in a stainless-steel mixing bowl and submerged in a mixture of 500 mL water and 500 mL Ecos. The bowl was agitated by hand for 3 min. Spinach leaves were then poured into a colander and rinsed with cold tap water for 30 s, air dried for 2 min, and homogenized. All homogenized samples were stored at 20°C until extraction. Figure 1 summarizes the treatment groups and processes.

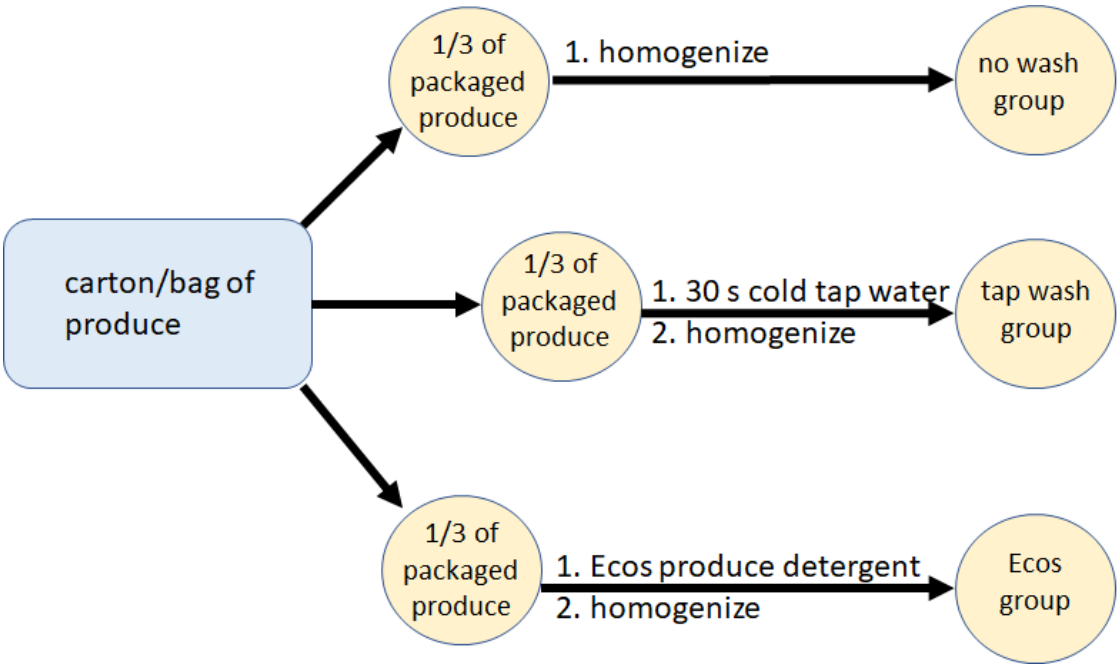


Figure 1. Schematic of treatment groups. This process was repeated for each produce type (strawberry, grape, spinach) and for each store (A, B, C) for a total of 36 homogenized samples.

EXTRACTION AND CLEANUP

Using a laboratory method published in Zhang et al., homogenized samples were thawed and extracted with acetonitrile, vortexed, and analyzed by liquid chromatography tandem mass spectrometry (LC-MS/MS) to measure the concentrations of azoxystrobin, fluoxastrobin, pyraclostrobin, and trifloxystrobin (Zhang et al. 2016). In short, 10 ng of d4-azoxystrobin and d3-pyraclostrobin were added to pre-weighted samples (1 g solid, 1 g juice for grape and strawberry samples; 2 g solid for spinach samples) to serve as an internal standard. Approximately 4 mL of acetonitrile was added, and samples were sonicated for 5 min and then centrifuged for 5 min. The supernatant was transferred to a clean test tube and an additional 4 mL acetonitrile was added to the sample, which was subsequently sonicated and centrifuged 2 more times to generate a total of 12 mL acetonitrile extract for each sample. Extracts were concentrated using an N-EVAP until near dryness.

After rinsing each sample with 2 mL hexane, samples were loaded into ENVI Florisil SPE tubes for solid phase extraction. Samples were first washed with 4 mL hexane. Then, extracts were collected from the SPE tubes with approximately 12 mL of hexane as an eluent. The resulting eluent was dried using the N-EVAP. After adding 0.6 mL of 50%/50% methanol/water, each sample was spiked with 10 ng of d6-linuron, filtered through 0.2 μm Nylon mini-uniprep, and analyzed using LC-MS/MS as reported in Zhang et al. 2016**.**

QUALITY ASSURANCE AND QUALITY CONTROL

In October 2019, three cartons of generic strawberries were purchased from Store A to serve as both a second sample and to assess method performance. The strawberries from all three cartons were mixed together to create one large pooled sample. Strawberries were divided up into three treatment groups (7-8 strawberries per group) as described above. Briefly, these samples included three unwashed, three tap washed, and three Ecos treated replicates for a total of 9 additional samples. One replicate in each treatment group was spiked with approximately 100 μL of a mixture of each strobilurin (0.1242 ng/μL azoxystrobin, 1.008 ng/μL pyraclostrobin, 0.124 ng/μL trifloxystrobin, and 0.1368 ng/μL fluoxastrobin) to assess method recoveries and potential matrix effects.

Lab processing blanks (n=3) were also analyzed with all samples. The method detection limit for each analyte was calculated by taking three times the standard deviation of these blanks and dividing the value by the average mass of sample extracted (2 g). All samples were blank corrected.

Statistical Analysis

Analysis of variance (ANOVA) tests were conducted to test the difference in mean concentration (ng/g) between treatment groups according to produce and strobilurin compound. Specifically, two tests were conducted to assess the effect of washing treatment. One test was conducted with pyraclostrobin residue on grapes and one with trifloxystrobin residue on strawberries. Statistical significance was considered to be p-value less than 0.05.

EXPOSURE AND RISK ESTIMATES

The USDA Total Diet Study (TDS) was used as a basis to estimate overall human health risk from exposure to these compounds via ingestion of produce (Center for Food Safety and Applied Nutrition 2018). Using standard US EPA risk analysis methods, hazard quotient values were calculated for a child, adult female, and adult male using the following equation (US EPA 2015):

$$\text{Hazard Quotient (HQ)} = \frac{\text{Exposure Concentration}}{\text{Reference Dose (RfD)}}$$

Exposure concentration, which is the amount of fungicide that someone would be exposed to over a day, was determined using the maximum residue concentration observed on select produce samples and a consumption rate based on the USDA daily recommended intake of produce. These values were also corrected for the average mass of a child, adult female, and adult male ("Exposure Factors Handbook 2011 Edition (Final Report)" 2011).

The acute reference dose (RfD) and chronic RfD values, which are estimates of daily exposure that is not associated with significant risk of adverse human health effects over a lifetime, used in these calculations were sourced from the current scientific literature ("Pyraclostrobin; Pesticide Tolerances" 2015).

Results

Pyraclostrobin, trifloxystrobin, and azoxystrobin were the primary strobilurin compounds detected on the strawberry, grape, and spinach samples. Overall, many samples had residue levels below the method detection limit (MDL) and were therefore considered as non-detects. Many values were also only slightly above the MDL, which suggests that residue is not due to intentional application of the fungicides. Furthermore, generic varieties tended to have higher concentrations than organic varieties (Tables 2-4, Figures 2-3). For instance, when detected, pyraclostrobin concentrations were as much as 600 times larger on generic strawberries and 100 times larger on generic grapes than on their organic counterparts.

Trifloxystrobin concentrations were almost 1,000 times larger on generic strawberries than on organic in some cases.

For strawberry samples specifically, trifloxystrobin was the main strobilurin detected, although one sample also had a high pyraclostrobin residue (Table 2). In grape samples, pyraclostrobin was the contaminant with the highest residue levels (Table 3). These higher residue concentrations suggest that produce was deliberately applied with the strobilurin compounds. For spinach samples, there were generally very low residues (Table 4).

Table 2. Azoxystrobin, fluoxastrobin, pyraclostrobin, and trifloxystrobin residue concentrations measured on the generic and organic varieties of strawberry samples. All values "< MDL" were considered non-detect values. Samples from Store A1 are those collected and processed during the initial sampling events, while those from Store A2 are from the quality assurance and quality control phase. Store A2 values are averages of the two samples replicates for each treatment group.

Strawberries					
Store	Variety	Fungicide			
		Azoxystrobin	Fluoxastrobin	Pyraclostrobin	Trifloxystrobin
A_1	Generic	<MDL	<MDL	54.04	29.40
	Organic	<MDL	<MDL	0.09	0.02
A_2	Generic	<MDL	<MDL	<MDL	<MDL
B	Generic	<MDL	<MDL	0.06	3.03
	Organic	<MDL	<MDL	0.07	0.03
C	Generic	0.06	<MDL	0.11	12.98
	Organic	<MDL	<MDL	0.08	0.03
MDL_1 (ng/g)		0.02	0.01	0.02	0.01
MDL_2 (ng/g)		0.06	0.05	0.09	0.05

Table 3. Azoxystrobin, fluoxastrobin, pyraclostrobin, and trifloxystrobin residue concentrations on generic and organic varieties of grape samples. All values "< MDL" were considered non-detect values.

Grapes					
Store	Variety	Fungicide			
		Azoxystrobin	Fluoxastrobin	Pyraclostrobin	Trifloxystrobin
A	Generic	0.19	<MDL	<MDL	0.06
	Organic	<MDL	<MDL	<MDL	1.87
B	Generic	0.03	<MDL	23.95	<MDL
	Organic	<MDL	<MDL	<MDL	0.41
C	Generic	<MDL	<MDL	34.84	0.03
	Organic	0.45	<MDL	<MDL	0.21
MDL (ng/g)		0.02	0.03	0.33	0.02

Table 4. Azoxystrobin, fluoxastrobin, pyraclostrobin, and trifloxystrobin residue concentrations on generic and organic varieties of spinach samples. All values "< MDL" were considered non-detect values.

Spinach					
Store	Variety	Fungicide			
		Azoxystrobin	Fluoxastrobin	Pyraclostrobin	Trifloxystrobin
A	Generic	0.58	<MDL	0.16	<MDL
	Organic	<MDL	<MDL	<MDL	<MDL
B	Generic	<MDL	<MDL	0.08	<MDL
	Organic	<MDL	<MDL	0.05	<MDL
C	Generic	0.04	<MDL	0.10	<MDL
	Organic	<MDL	<MDL	<MDL	<MDL
MDL (ng/g)		0.02	0.01	0.02	0.01

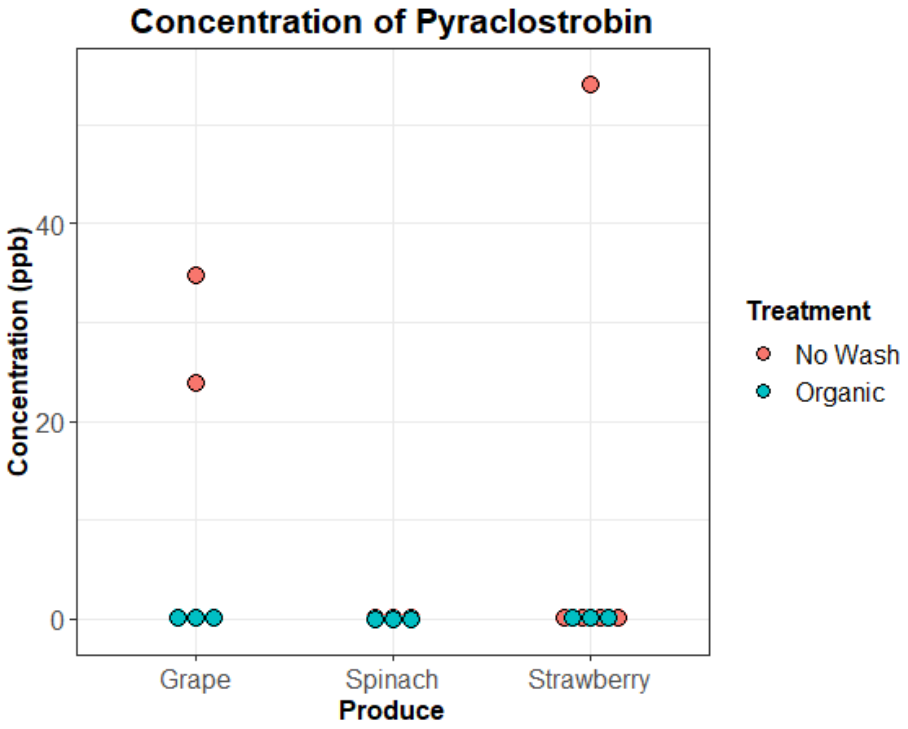


Figure 2. Concentrations of pyraclostrobin on generic, unwashed produce and organic produce varieties. For visualization, samples that were <MDL were plotted using a value equivalent to ½ of the MDL in ng/g.

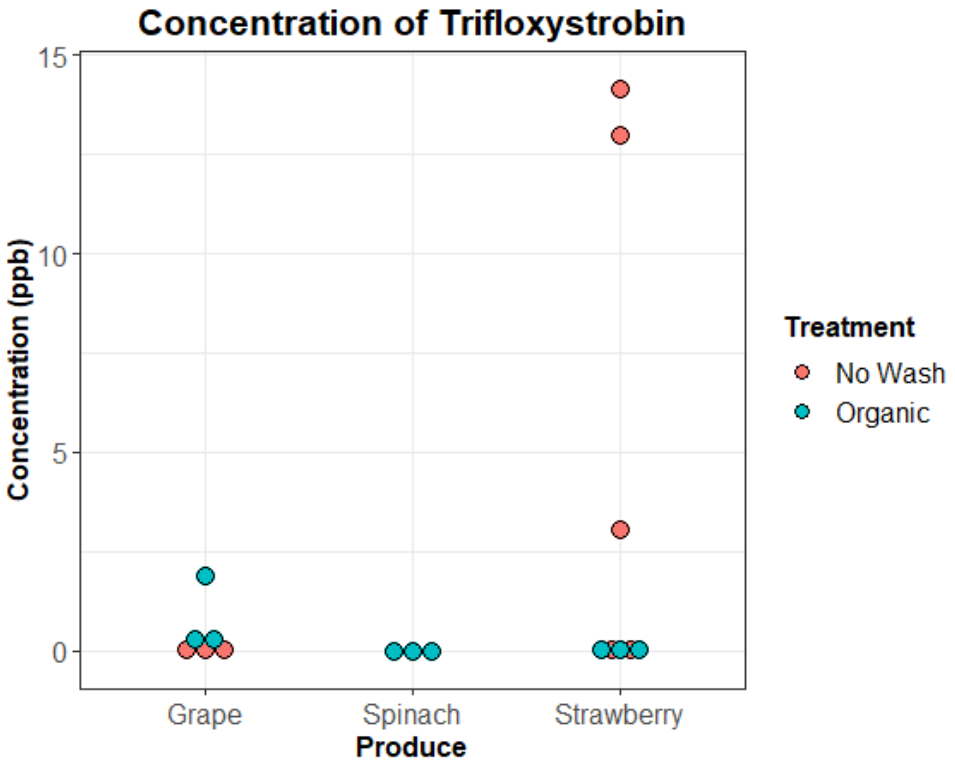


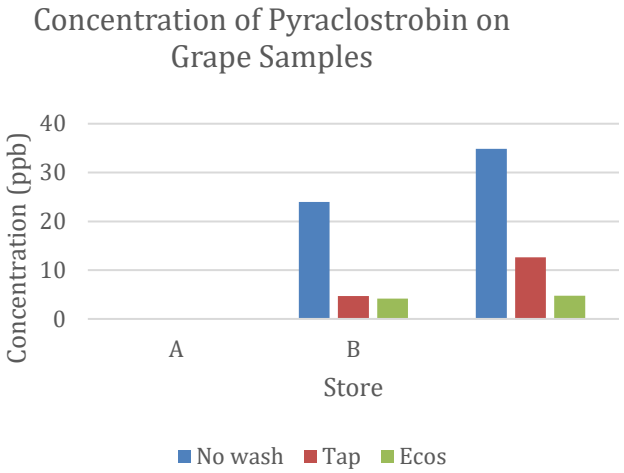
Figure 3. Concentrations of pyraclostrobin on generic, unwashed produce and organic produce varieties. Note that ½ of the MDL in ng/g is shown for non-detect concentration values.

EFFECTS OF WASHING

Strobilurin residue was also measured on generic produce following two different washing treatments, a cold-water rinse and a treatment with a produce detergent (Ecos), to compare the effectiveness of these two methods. The average percent removal of pyraclostrobin residue on grape samples (collected from Stores B and C only) was greater with the Ecos detergent treatment (85%) than with the tap water rinse (71%) as shown in Figure 4. On the other hand, the average percent removal of trifloxystrobin on strawberry samples was greater with the tap water rinse (52%) than with the Ecos detergent treatment (45%, excluding the elevated residue sample from Store C; Figure 5).

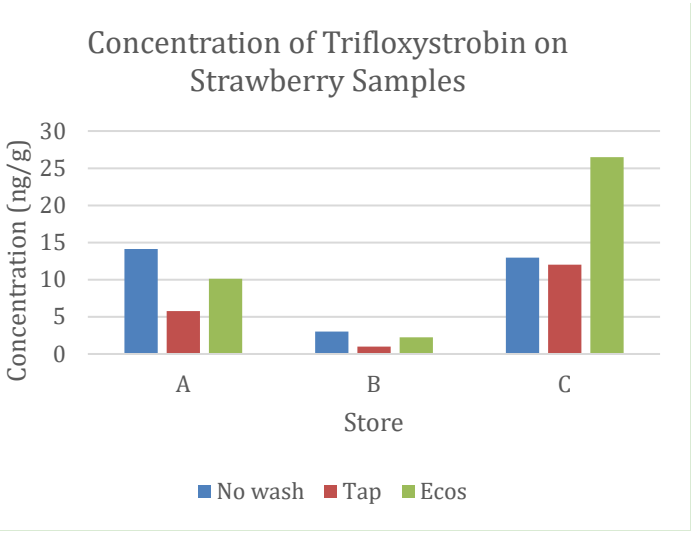
ANOVA analyses were conducted to test the statistical difference between residue concentrations on produce according to treatment. For grapes, pyraclostrobin residue levels were not statistically different. A post hoc Tukey HSD test, while also not statistically significant, suggests that on average both the Ecos and tap wash treatments had lower residue levels than the unwashed grapes; Ecos-treated samples had lower residue levels than tap washed ones. For strawberries, trifloxystrobin residue levels were not statistically different among treatment groups. Again, though not statistically significant, post hoc Tukey tests indicate that, on average, samples that were rinsed with tap water had lower

trifloxystrobin levels than those that were not washed and those that were treated with the Ecos produce detergent (See Appendix Exhibit D for full ANOVA analysis results).



Grapes - Pyraclostrobin			
Store	Treatment	Concentration (ng/g)	% Removal
B	No wash	23.95	-
	Tap	4.67	80.50
	Ecos	4.16	82.64
C	No wash	34.84	-
	Tap	12.62	63.79
	Ecos	4.77	86.32

Figure 4. Concentration and percent removal of pyraclostrobin residue on grapes collected from Stores B and C, according to treatment. Data from A is not included due as concentrations were below the MDL. Note that any non-detect data shown represents ½ of the MDL in ng/g.



Strawberries - Trifloxystrobin			
Store	Treatment	Concentration (ng/g)	% Removal
A	No wash	29.40	-
	Tap	5.75	80.43
	Ecos	10.12	65.59
B	No wash	3.03	-
	Tap	0.99	67.27
	Ecos	2.25	25.89
C	No wash	12.98	-
	Tap	12.03	7.35
	Ecos	26.47	-103.88

Figure 5. Concentration and percent removal of trifloxystrobin residue on strawberries collected from Stores A, B, and C according to treatment. Note that any non-detect data shown represents ½ of the MDL in ng/g.

HAZARD QUOTIENTS

As pyraclostrobin had the largest residue levels on grapes and strawberries, respectively, these values were selected to estimate human exposure and risk. Exposure concentration measurements for children, women, and men were calculated using these observed values and correcting for body weight and consumption of produce in one day.

For children 2-3 years old with an average mass of 13.1 kg, the recommended daily intake of fruit is 1 cup of fruit, which is equal to approximately 92 g of grapes and 168 g of strawberries. For women, the recommendation is 1.5 cups of fruit, which is equal to 138 g of grapes and 252 g of strawberries. For men, the recommendation is 2 cups of fruit, which is equal to 184 g of grapes and 336 g of strawberries. (United States Department of Agriculture 2015a; "Grapes | SNAP-Ed Connection" n.d.; "Strawberries | SNAP-Ed Connection" n.d.). Both male and female adults are assumed to have an average mass of 70 kg.

The lowest acute dietary RfD for pyraclostrobin is 0.05 mg/kg/day, based on developmental toxicity in rabbits. The lowest chronic dietary RfD is 0.034 mg/kg/day, based on carcinogenicity in rats. ("Pyraclostrobin; Pesticide Tolerances" 2015).

For both the grape and strawberry samples, acute and chronic hazard quotient values are less than one for children, women, and men. This suggests that there is negligible risk of adverse human health effects from pyraclostrobin exposure via ingestion of grapes and strawberries, respectively (Table 5).

Table 5. Hazard quotients calculated for pyraclostrobin exposure scenarios. Exposure estimates utilized the highest concentration observed per produce type and under the assumption that children, adult females, and adult males consume the recommended daily intake of grapes and strawberries.

Produce	Maximum Observed Residue Concentration (ng/g)	Exposure Concentration (mg/kg-day)		Acute RfD (mg/kg-day)	Chronic RfD (mg/kg-day)	Acute HQ	Chronic HQ
Grape	34.84	Child	2.45×10^{-4}	0.05	0.034	0.0049	0.0072
		Adult Female	6.87×10^{-5}			0.0014	0.02
		Adult Male	9.16×10^{-5}			0.0018	0.0027
Strawberry	54.04	Child	6.93×10^{-4}	0.05	0.034	0.014	0.02
		Adult Female	1.95×10^{-4}			0.0039	0.0057
		Adult Male	2.59×10^{-4}			0.0052	0.0076

Discussion

This study quantified the potential exposure to strobilurin fungicides that people face when consuming strawberries, grapes, and spinach purchased from three grocery stores local to Durham, NC. Such exposure data is important given that little information currently exists for this new class of compounds, has implications for consumers unable to pay for organic produce, and provides insight on overall health of the population. Because many samples had residue values either below the MDL or slightly above the MDL, it is likely that these residues are not due to intentional application of the fungicides. Instead, the compounds' presence may be due to contamination during processing, packaging, and handling of produce before reaching grocery stores. Alternatively, these low levels could also be attributed to fungicide drift from separate areas that received application during the growing and harvesting seasons. However, the relatively higher residue concentrations of pyraclostrobin on grapes and trifloxystrobin on strawberries suggest that these produce samples were intentionally applied with the respective fungicides.

Results from this study indicate that organic produce varieties have lower strobilurin fungicide residue levels. This corroborates previous research findings that organic produce varieties typically have lower pesticide residues (Winter and Davis 2006; Baker et al. 2002; Pearson et al. 2016). Because strobilurin compounds have been linked to metabolic syndromes and transcriptionally mimic autism spectrum disease and neurodegenerative disease (in cell cultures), consuming organic produce therefore may reduce the risk of such adverse human health outcomes (Pearson et al. 2016; Luz et al. 2018).

IMPACTS OF WASHING PRODUCE BEFORE CONSUMPTION

Results from this study do indicate that washing affects the residue concentrations; however, there is no clear pattern between the tap water rinse and the Ecos detergent treatments. On average, the Ecos produce detergent removed a higher percentage of pyraclostrobin on grapes samples, while the tap water rinse removed a higher percentage of trifloxystrobin on strawberry samples. However, neither treatment was able to remove 100% of the residue, and organic varieties still had lower residue levels. To truly minimize exposure to these strobilurin fungicides, one should purchase organic varieties, though the differences in overall risk may not be significant, as discussed below.

These findings also support recent postulations that log K_{ow} or water solubility properties alone may not be sufficient in predicting how well compounds wash off produce. Although limited by a small sample size, the calculated percent removal values show no clear pattern in changes in residue levels by treatment. For instance, of the four strobilurin compounds in the study, trifloxystrobin has the highest log K_{ow} value and therefore, hypothetically, should have the lowest removal rate by the tap treatment. However, results demonstrate that this was not necessarily the case.

COMPARISON TO THE USDA PESTICIDE DATA PROGRAM (PDP)

The USDA Pesticide Data Program (PDP) collects data on pesticide residue on commodity agricultural items. Its goal is to create a database that can be used to assess dietary exposure to pesticides, inform global marketing of US agricultural products, and guide governmental agencies in making regulatory decisions ("The Pesticide Data Program" 2015). Using this database, the values obtained from this study were compared to historical trends on strobilurin residues on crops. The temporal trend data from PDP suggest that azoxystrobin, fluoxastrobin, pyraclostrobin, and trifloxystrobin are infrequently detected on grapes, spinach, and strawberries that were analyzed from 2008 to 2016, suggesting varying agricultural application patterns (Figures 6-8). It should be noted that the PDP did not collect data in all years for certain strobilurin and commodity combinations.

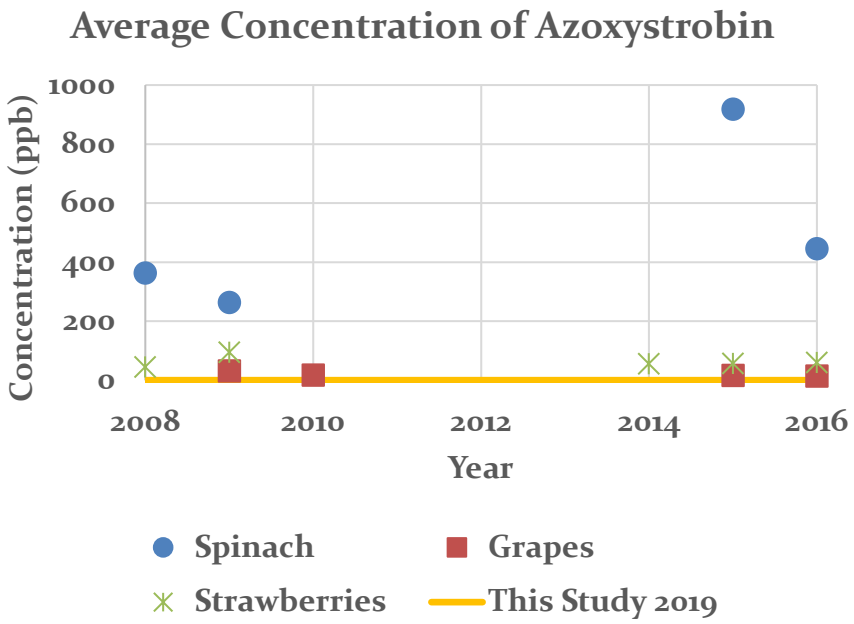


Figure 6. Average concentration of azoxystrobin residue levels from samples with positive detects from the PDP dataset in 2008-2016. The yellow line represents the maximum residue level observed in this study on grapes, spinach, and strawberries.

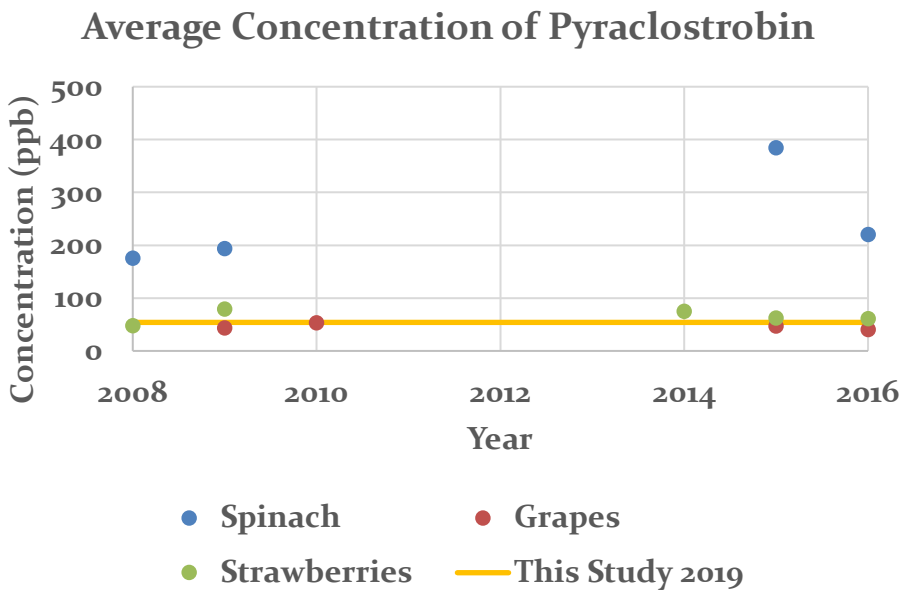


Figure 7. Average concentration of pyraclostrobin residue levels from samples with positive detects from the PDP dataset in 2008-2016. The yellow line represents the maximum residue level observed in this study on grapes, spinach, and strawberries.

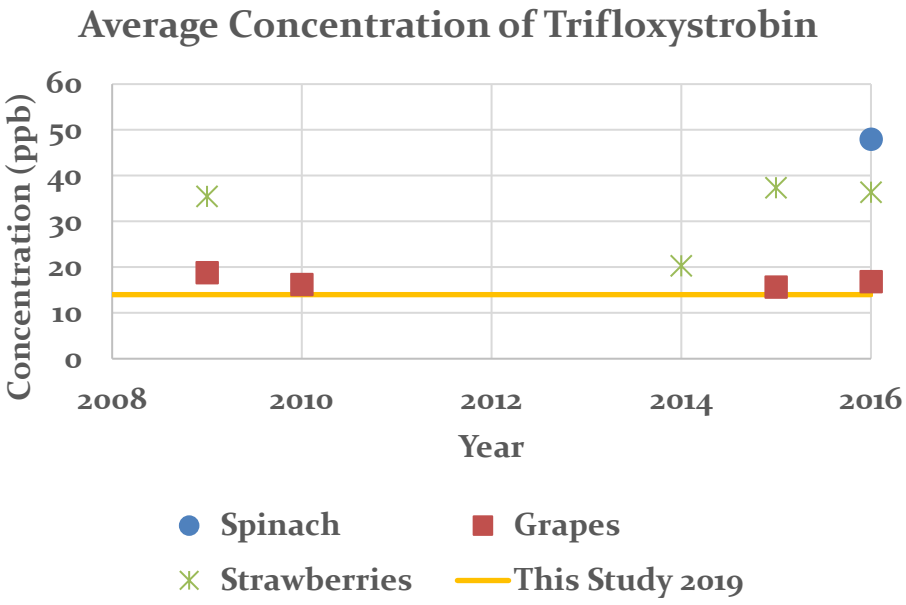


Figure 8. Average concentration of trifloxystrobin residue levels from samples with positive detects from the PDP dataset in 2008-2016. The yellow line represents the maximum residue level observed in this study on grapes, spinach, and strawberries.

Many of the average values from the PDP data set, especially in recent years, are similar to the results from this study. Additionally, the detection frequencies are rather low in both the PDP and this study's data. From 2008 to 2016, the PDP detection frequency of azoxystrobin in spinach, grapes, and strawberries ranged from 4-6%, 4-5%, and 10-20%, respectively; for pyraclostrobin, detection frequency ranged from 6-10%, 37-47%, and 42-53%, respectively; for trifloxystrobin, the detection frequency ranged from zero to less than 1%, 25-34%, and 0-12%, respectively. Fluoxastrobin was not detected in either study.

The PDP data reflect an apparent decline in industrial application of strobilurin fungicides. Such a trend may be attributed to the growing concerns of exposure effects. However, key data is missing from 2017 and 2018 that would strengthen this hypothesis of industry's apparent decreasing use in these strobilurin fungicides. See Appendix Exhibit E for PDP summary data tables.

INTERPRETATION OF HAZARD QUOTIENTS

Regardless of the produce or treatment, total exposure to individual compounds via ingestion does not appear to pose a significant risk. Hazard quotients calculated for children, adult females, and adult males based on highest observed concentration level were significantly less than 1, indicating negligible risk of adverse human health outcomes (Table 5). Based on this study's findings, a strong recommendation to purchase organic over generic varieties (or vice versa) could not be made. In other words, the price premium for organic may not be worth it in the eyes of the consumer in regard to exposure to azoxystrobin, fluoxastrobin, pyraclostrobin, and trifloxystrobin. Consumers also may not have to spend additional money on the Ecos produce detergent, since our data suggests it is not more efficient at removing residues than just rinsing with tap water. Granted, these conclusions are based on some assumptions in the hazard quotient calculations, as well as small sample size. Assuming that an individual only consumes a single type of produce, consumes the total recommended daily amount of fruit, and does not have other routes of exposure, for example, may result in over- or underestimated risk. A larger study would provide more information on differences in residue removal according to treatment.

This study is not without limitations. Future research using larger sample sizes would be needed to more fully describe the effects of washing produce with tap water and Ecos produce detergent with statistical significance. This study could also be expanded to include other types of produce and consumer handling methods prior to consumption. For instance, it did not include other berries that may be prone to fungicide application, or other possible consumer washing techniques (i.e., soaking produce in water, drying produce with a paper towel, boiling produce) that may change exposure levels prior to consumption. Lastly, these results are only indicative of the four strobilurin compounds tested here.

Residues of other pesticides, especially newer ones that may replace strobilurins as they receive negative public attention, cannot be predicted from these results.

Conclusion

Strobilurin fungicides are a relatively new class of pesticide compounds that have increasingly become environmental contaminants of concern. Recent research has highlighted both the growing use of strobilurin fungicides and possible links to adverse human health outcomes from exposure. Because ingestion is a common route of exposure to pesticides, this study aimed to quantify residue levels of four common strobilurin compounds (azoxystrobin, fluoxastrobin, pyraclostrobin, and trifloxystrobin) on produce (grapes, strawberries, spinach) to improve understanding of possible exposure from food consumption.

Results indicated that consumption of produce with the residue levels observed here would not result in an exposure level above reference dose value that reflects an increased risk for harm. Furthermore, organic produce varieties generally had lower residue levels than generic varieties. At the same time, treating produce before ingestion can lower residue levels. However, minimal differences between washing with tap water and treating with Ecos produce detergent were observed, and potentially suggests that a wash with detergent is not needed for this class of fungicides. Furthermore, results are in line with the pesticide residue database by the USDA Pesticide Data Program (PDP), although data missing from 2017 and 2018 would serve as more representative comparisons for compound use.

Future research in this field should consider larger sample sizes, a wider variety of produce types for analysis, and other food preparation techniques that consumers may use prior to food consumption. Just as important, analysis of produce for residues of other pesticides will be necessary to remain informed on human exposures. Industry continues to develop and use new pesticide compounds, and, as the case of strobilurins has shown, despite the US EPA approving these emerging chemicals for use, they may still present risks to human health. Continuing to collect information on exposure to these potentially harmful chemicals would allow for timely risk estimates related to the ingestion of foods to which pesticides are applied and help ensure the safety of the general population.

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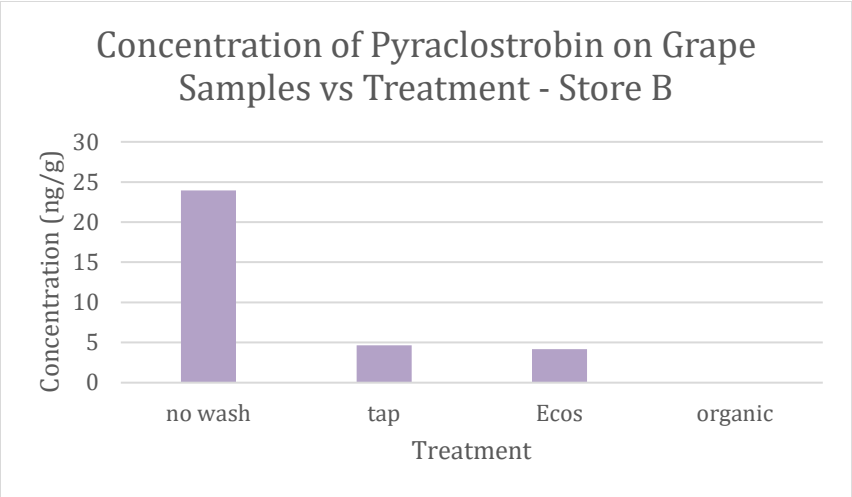
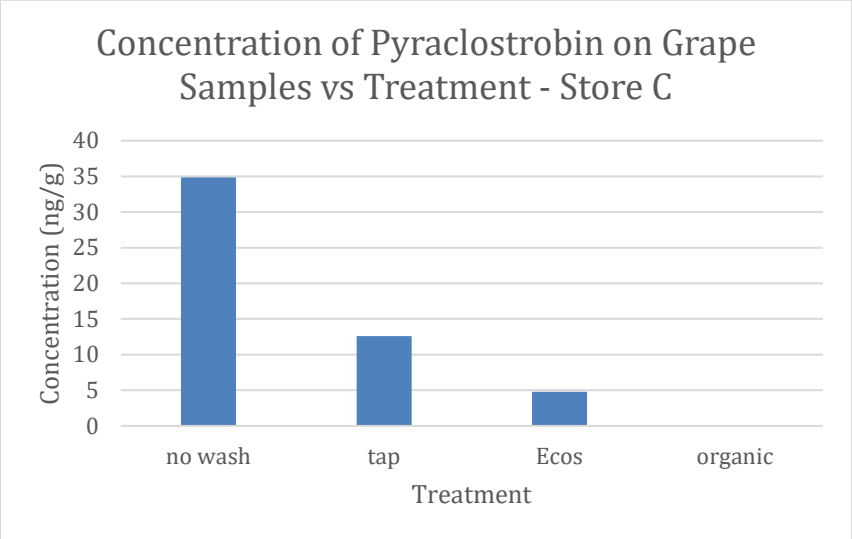
Appendix

Exhibit A. Strobilurin concentrations on select grape samples.





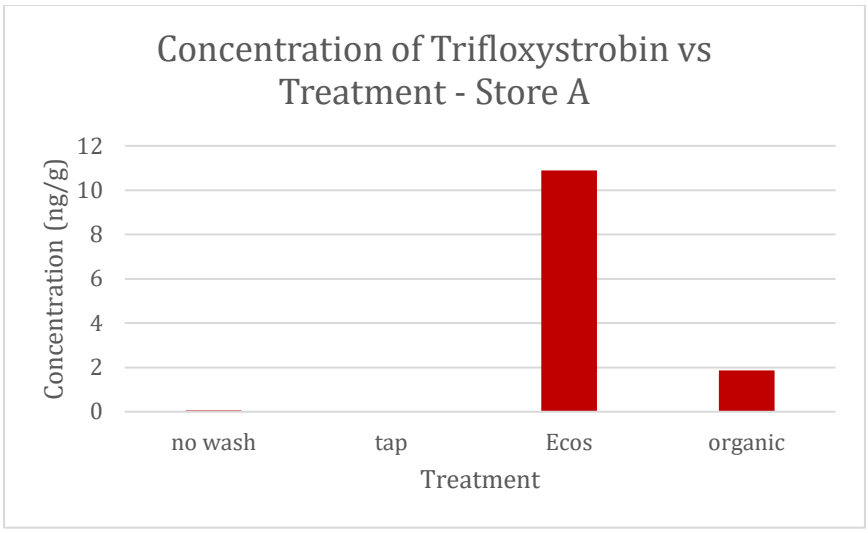


Exhibit B. Strobilurin concentrations on select spinach samples.

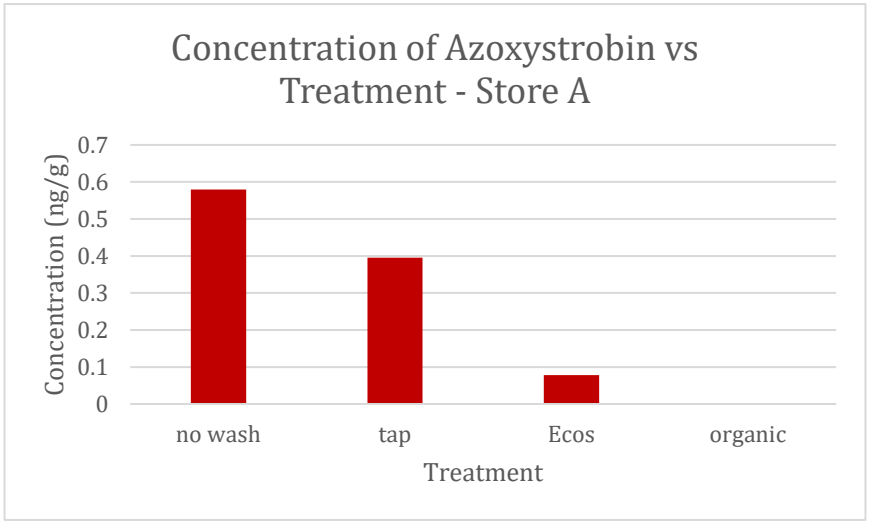
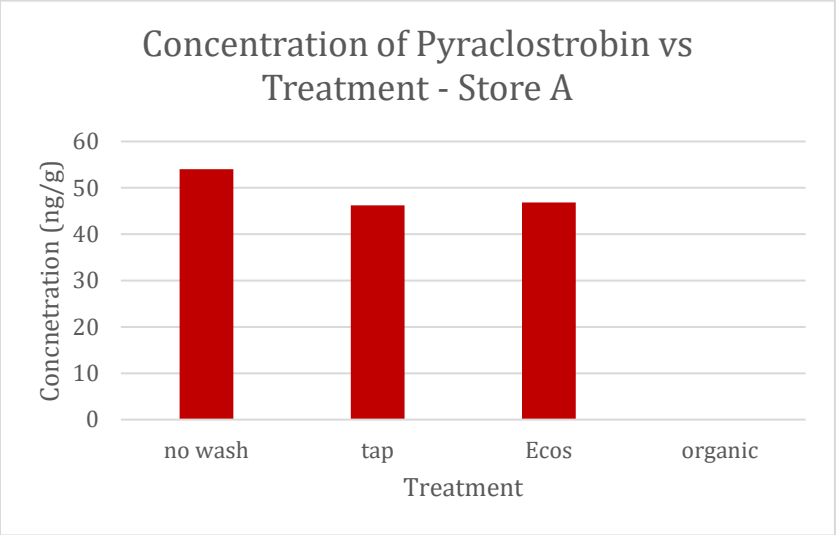
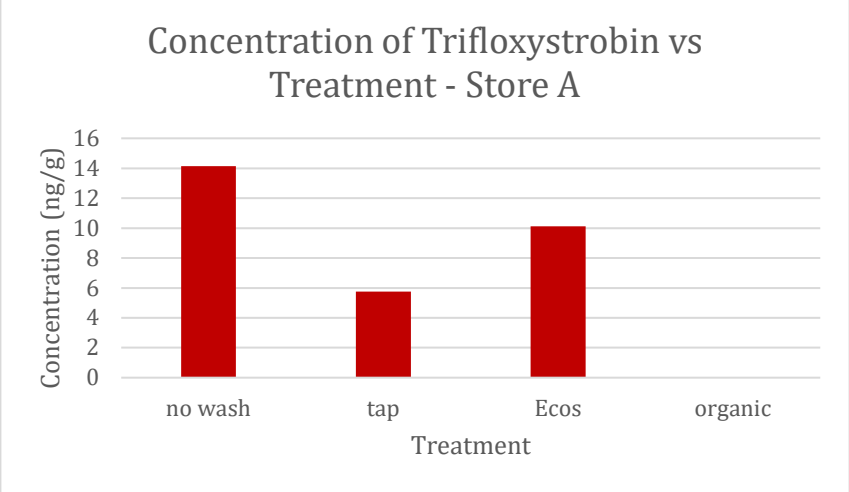
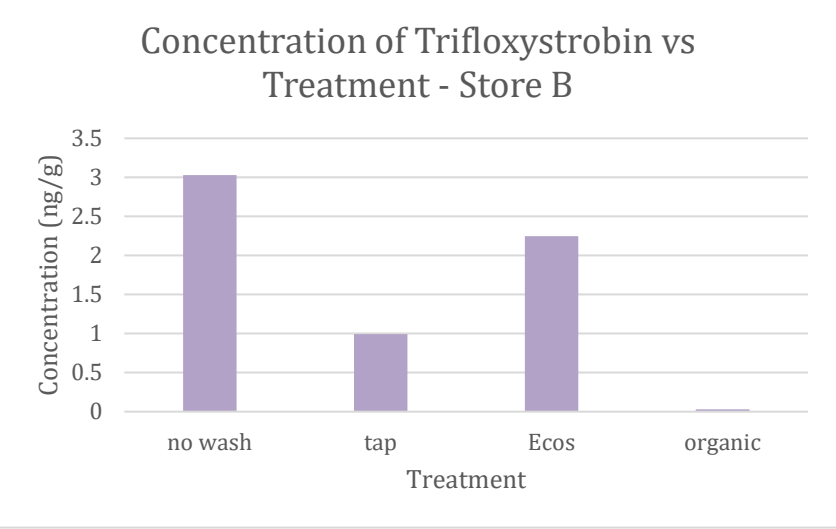


Exhibit C. Strobilurin concentrations on select strawberries samples.







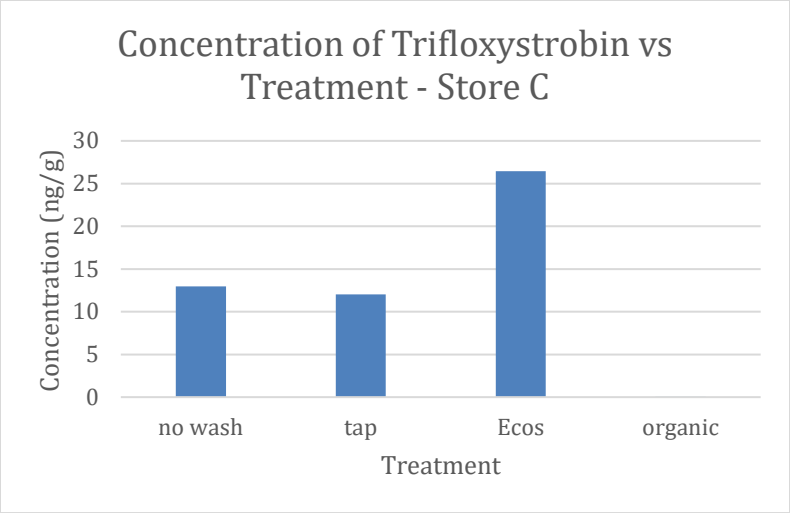


Exhibit D. ANOVA analysis results.

Grapes: pyraclostrobin

	Df	Sum Sq	Mean Sq	F value	p-value (Pr(>F))
Treatment	2	475.6	237.8	1.97	0.22
residuals	6	725.6	120.9		

Tukey multiple comparisons of means, 95% family-wise confidence level

	diff	Lwr	Upr	P adj
No wash-Ecos	16.62	-10.93	44.17	0.23
Tap-Ecos	2.79	-24.76	30.34	0.95
Tap-no wash	-13.84	-41.39	13.71	0.34

Strawberries: trifloxystrobin

	Df	Sum Sq	Mean Sq	F value	p-value (Pr(>F))
Treatment	2	40.5	20.23	0.3	0.75

residuals	12	809.5	67.46		

Tukey multiple comparisons of means, 95% family-wise confidence level

	diff	Lwr	Upr	P adj
No wash-Ecos	-1.74	-15.50	12.12	0.94
Tap-Ecos	-4.01	-17.87	9.85	0.73
Tap-no wash	-2.27	-16.13	11.58	0.90

Exhibit E. PDP summaries by year.

2016

Pesticide Name	Commodity	Number of Samples Analyzed	Number of Samples with Detects	Pct of Samples with Detects	Min Detect	Max Detect	LOD Range	pp_	EPA Tolerance (ppm)
Azoxystrobin	Grapes	708	32	4.5	0.005	0.0485	0.003	M	2
Azoxystrobin	Spinach	707	37	5.2	0.002	4.4	0.001 - 0.01	M	30
Azoxystrobin	Strawberries	530	88	16.6	0.0013	0.64	0.0012	M	10
Fluoxastrobin	Spinach	707	0				0.0012 - 0.015	M	NT
Fluoxastrobin	Strawberries	530	1	0.2	0.0016	0.0016	0.0012	M	1.9
Pyraclostrobin	Grapes	708	269	38	0.005	0.2293	0.003	M	2
Pyraclostrobin	Spinach	707	71	10	0.0018	1.7	0.0011 - 0.005	M	29
Pyraclostrobin	Strawberries	530	259	48.9	0.0013	0.83	0.0012	M	1.2
Trifloxystrobin	Grapes	708	175	24.7	0.005	0.1781	0.003	M	2
Trifloxystrobin	Spinach	707	1	0.1	0.048	0.048	0.001 - 0.005	M	30
Trifloxystrobin	Strawberries	530	63	11.9	0.0015	0.14	0.0012	M	1.5

2015

Pesticide Name	Commodity	Number of Samples Analyzed	Number of Samples with Detects	Pct of Samples with Detects	Min Detect	Max Detect	LOD Range	pp_	EPA Tolerance (ppm)
Azoxystrobin	Grapes	708	27	3.8	0.005	0.0444	0.003	M	2
Azoxystrobin	Spinach	708	43	6.1	0.002	16	0.001 - 0.0051	M	30
Azoxystrobin	Strawberries	706	76	10.8	0.0013	0.57	0.0012 - 0.0025	M	10
Fluoxastrobin	Spinach	708	0				0.0012 - 0.013	M	NT
Fluoxastrobin	Strawberries	706	6	0.8	0.0019	0.026	0.0012 - 0.0025	M	1.9
Pyraclostrobin	Grapes	708	323	45.6	0.005	0.3633	0.003	M	2
Pyraclostrobin	Spinach	708	62	8.8	0.0018	5	0.0011 - 0.002	M	29
Pyraclostrobin	Strawberries	706	300	42.5	0.0013	0.49	0.0012 - 0.0025	M	1.2

2014

Pesticide Name	Commodity	Number of Samples Analyzed	Number of Samples with Detects	Pct of Samples with Detects	Min Detect	Max Detect	LOD Range	pp_	EPA Tolerance (ppm)
Azoxystrobin	Strawberries	176	34	19.3	0.0031	0.37	0.0025	M	10
Fluoxastrobin	Strawberries	176	0				0.0025	M	1.9
Pyraclostrobin	Strawberries	176	82	46.6	0.0026	0.66	0.0025	M	1.2
Trifloxystrobin	Strawberries	176	6	3.4	0.0049	0.055	0.0025	M	1.1

No data was collected in 2011-2013.

2010

Pesticide Name	Commodity	Number of Samples Analyzed	Number of Samples with Detects	Pct of Samples with Detects	Min Detect	Max Detect	LOD Range	pp_	EPA Tolerance (ppm)
Azoxystrobin	Grapes	745	35	4.7	0.0025	0.088	0.0015 - 0.0025	M	1
Fluoxastrobin	Grapes	372	0				0.025	M	NT
Pyraclostrobin	Grapes	745	346	46.4	0.001	1.5	0.001 - 0.0015	M	2
Trifloxystrobin	Grapes	745	250	33.6	0.0025	0.25	0.0015 - 0.0025	M	2

2009

Pesticide Name	Commodity	Number of Samples Analyzed	Number of Samples with Detects	Pct of Samples with Detects	Min Detect	Max Detect	LOD Range	pp_	EPA Tolerance (ppm)
Azoxystrobin	Grapes	744	59	7.9	0.0025	0.24	0.0015 - 0.0025	M	1
Azoxystrobin	Spinach	744	42	5.6	0.0021	4.6	0.0015 - 0.002	M	30
Azoxystrobin	Strawberries	744	77	10.3	0.0025	0.96	0.0015 - 0.0025	M	10
Fluoxastrobin	Spinach	88	0				0.002	M	NT
Pyraclostrobin	Grapes	744	337	45.3	0.001	0.51	0.001 - 0.0015	M	2
Pyraclostrobin	Spinach	744	70	9.4	0.0025	2.9	0.0015 - 0.0025	M	29
Pyraclostrobin	Strawberries	744	324	43.5	0.001	0.61	0.001 - 0.0015	M	1.2
Trifloxystrobin	Grapes	744	211	28.4	0.0025	0.31	0.0015 - 0.0025	M	2
Trifloxystrobin	Spinach	744	0				0.0015 - 0.005	M	NT
Trifloxystrobin	Strawberries	744	10	1.3	0.0029	0.13	0.0015 - 0.0025	M	1.1

2008

Pesticide Name	Commodity	Number of Samples Analyzed	Number of Samples with Detects	Pct of Samples with Detects	Min Detect	Max Detect	LOD Range	pp_	EPA Tolerance (ppm)
Azoxystrobin	Spinach	744	28	3.8	0.0008	4	0.0005 - 0.002	M	30
Azoxystrobin	Strawberries	741	97	13.1	0.0005	0.48	0.0004 - 0.001	M	10
Pyraclostrobin	Spinach	744	46	6.2	0.002	1.7	0.001 - 0.0025	M	29
Pyraclostrobin	Strawberries	741	392	52.9	0.0008	0.61	0.0008 - 0.001	M	1.2
Trifloxystrobin	Spinach	744	0				0.001 - 0.005	M	NT
Trifloxystrobin	Strawberries	741	0				0.0004 - 0.001	M	1.1