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A Comparison of Pesticide Monitoring Programs, State vs. Federal

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A COMPARISON OF PESTICIDE MONITORING PROGRAMS, STATE VS. FEDERAL

by

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ABSTRACT

Exposure to pesticide residues continues to be a threat to both human and environmental health despite increased efforts in the agricultural industry to control end-product levels. Multiple government agencies routinely sample and screen common agricultural commodities (fruits and vegetables) for pesticide residues, albeit to do so they use different commodity sampling methods and satisfy different program objectives. Often, results of such screening programs are used in a supplementary fashion in human and environmental health studies, but rarely are the results studied against one another. Six years of archived data (narrowed down from 14) of two separate pesticide monitoring programs were isolated and matching quantitative data were compared against one another. Of particular interest are historical detections of various organochlorines, organophosphates, and organonitrates in common fruits and vegetables as well as detected concentrations of these compounds across both surveys. Historical outcomes were compared using linear regression models and t-tests of the matching detections to investigate trends in the pooled data over the various commodities sampled, chemical compounds detected, detection frequencies, and any effects potentially related to inherent characteristics of both the commodities or compounds. Nearly all t-tests indicated that mean detections of the surveys do not significantly differ at the 5% level; however, t-tests were more likely to detect significant differences as the number of observations grew. Roughly 25% of matrix-specific regression models could explain the variance of one survey's outcome on another with $r^2 > 0.90$, while nearly half of models had $r^2 > 0.50$.

Regressions of compound and matrix structural property effects against differences in survey outcomes were generally less reliable, but did show some trends in the models' slopes. While not conclusive, the results lay a foundation for future concentrated research and demonstrate the need for increased data sharing and cooperation between all State and Federal agencies, as much of their annual data can be very useful beyond its intended scope when examined conjunctively.

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LIST OF ABBREVIATIONS

ADI	Acceptable Daily Intake
AMS	Agricultural Marketing Service
EPA	Environmental Protection Agency
e-SIF	Electronic Sample Information Form
FDA	Food and Drug Administration
FSMA	Food Safety Modernization Act
FY	Fiscal Year
IPM	Integrated Pest Management
LOD	Limit of Detection
NASS	National Agricultural Statistics Service
PDP	Pesticide Data Program
POP	Persistent Organic Pollutant
ppb	parts per billion
ppm	parts per million
RSD	relative standard deviation
RMSE	root mean squared error
SCDA	South Carolina Department of Agriculture
SOP	Standard Operating Procedure
USDA	United States Department of Agriculture

CHAPTER 1

INTRODUCTION

Over the past several decades, populations in the developed world have become increasingly conscientious about the foods that they put into their bodies with respect to not only intake quantity but also the foods' inherent quality. This is reflected in surges in organic food production and revenue (Sahota 2008) and the increase in frequency and popularity of small urban markets where artisan type foods and general produce from surrounding rural communities and small urban farms can be purchased (Gillespie et al. 2007). Through direct communication with vendors in these types of environments, consumers can learn a great deal about the processes involved with generating the various foodstuffs, as well as specific ingredients and any growth-control mechanisms involved. What may be of little concern to 'non-organic' consumers is the application of numerous pesticides involved in the harvest of their produce (i.e. fruits and vegetables) and the subsequent processes used to cleanse the food of any residues before it is brought for sale, whether at an urban farmers' market or a traditional grocery retail store. The consumer may take a proactive approach and ensure their food is washed and prepared to subjective standards prior to eating. However, on the other hand, perhaps "ignorance is bliss" and consumers would either rather not know or do not care to put forth the effort into discovery of exactly how their produce is harvested. The middle of the road approach might be rather to assume that one or more government agencies are using taxpayer monies to survey the food supply so as to adequately ensure that food available

for sale contains only trace levels of pesticide residues, if any at all. This study is a comparison of the historical outcomes of two different pesticide survey methods to gauge the efficacy of State pesticide monitoring procedures as well as to make inferences on the nation's food supply regarding levels of pesticide residues to which the average person is being exposed. The study is intended to test the hypothesis that the outcomes of these pesticide monitoring programs produce similar results with respect to the individual chemicals detected in various commodities, the frequency with which they are detected, and their average detected concentrations. One survey uses a robust statistical model to create a statistically defensible depiction of the nation's food supply. For the purposes of this study, such a designed survey is considered the "national standard." Therefore, detections made by any other survey (which does not employ a robust statistical model) should fall within the national standard's estimates more often than they do not. Significant deviations from the national standard may offer insights into shift effects caused by the differences in the surveys' sampling procedures. If another survey differs significantly from the national standard, the two outcomes may still be correlated so that the outcome of one could be used to predict the outcome of the other.

CHAPTER 2

LITERATURE REVIEW

Market Basket Survey

One of the sampling methods of interest to this study is known as the market basket survey. The South Carolina Department of Agriculture (SCDA) and analogous State agencies nationwide employ the market-basket survey in efforts to randomly screen produce for the presence of pesticide residues. In a typical market basket survey, a sample collector is given the liberty to choose from any of the available produce for sale at a retail store as if he/she were a regular consumer. Fresh commodities are most often collected for analysis, however, frozen commodities as well as canned goods may occasionally be sampled. The goal of pesticide residue analysis via the market basket survey is to provide a weekly picture of the levels of pesticides the average consumer is being exposed as part of their dietary intake. The market basket survey is not an effective method of preventing exposures to unusually high levels of pesticides, however, because by the time analysis is complete, the remaining commodities of sampled lots have already been sold.

Data associated with the market basket method is often utilized as a research tool in literature and across many scientific disciplines. For example, large government health departments may utilize market basket data to study average grocery prices as compared to household incomes and average grocery bill amount per month

(Northern Territory Department of Health 2014). Scholars also use market basket survey data to investigate not only levels of pesticide residues in various agricultural commodities (Newsome et al. 2000; Bempah et al. 2012), but also other food contaminants such as trace levels of metals like lead, cadmium, copper, zinc, and arsenic (Radwan and Salama 2006; Williams et al. 2007).

Pesticide Data Program

The Pesticide Data Program (PDP) employs a different method of screening agricultural commodities for pesticide residue levels. In this annual survey sponsored by a branch of the U.S. Department of Agriculture, state population figures and other census data are used to determine a schedule for sampling commodities before they are distributed to retail locations. Sampled commodities are also predetermined prior to collection. That is, sample collectors in this survey do not have the freedom to sample whichever commodities they choose as compared to the market basket method. Rather, they are sent to specific locations and are told how much of each commodity of interest to collect.

Much like the market basket survey, PDP data has also been used in recent scientific literature. Most often, PDP data is used as a complementary or supplementary dataset for identifying historical trends of human pesticide exposure. For example, in 2002, Baker et al. investigated differences among three agricultural harvesting techniques with respect to pesticide residues detected using data from the PDP, the California Department of Pesticide Regulation, and a private testing organization. Several studies have also either used PDP generated data directly or as a reference in recent years to try

to quantify human exposure to various pesticides in concentrated geographical areas (Lu et al. 2006; Schechter et al. 2010).

Food Safety Modernization Act (2011)

Americans experienced a surge in foodborne illness within the first decade of the 21st century. There were an estimated 9.4 million annual occurrences of foodborne illnesses caused by 31 major known pathogens alone (CDC.gov; “Estimates of Foodborne Illness in the United States”). Additionally, some studies estimated another 38.4 million annual episodes of foodborne illness were caused by “unspecified agents” (Scallan et al. 2011). Coupled with these statistics, there had been increasing bioterrorism concerns among the American public after the attacks on the World Trade Center in New York City in 2001. As a result, Congress and President Obama’s first administration worked together to propose the first major overhaul of the nation’s food safety laws since 1938, the Food Safety Modernization Act (FSMA) of 2011 (National Sustainable Agriculture Coalition; “Overview and Background”). According to the FDA, the regulating authority of FSMA, the legislation “aims to ensure the U.S. food supply is safe by shifting the focus from responding to contamination to preventing it” (FDA.gov; “FDA Food Safety Modernization Act”).

Surprisingly, the FSMA “does not address food safety risks from genetically engineered crops, pesticide use, or antibiotic resistance” (National Sustainable Agriculture Coalition; “Overview and Background”). Apparently, the focus of the FSMA is on microbial pathogen contamination (such as Salmonella and E. coli) which would have the potential to adversely affect large numbers of people across the country from acute exposures (i.e. shredded lettuce contaminated with E. coli distributed to grocery

stores and/or restaurants in several geographic regions). Despite empirical evidence which suggests both long and short term pesticide exposures are associated with many chronic human health conditions (some examples will be discussed in the next section), the writers of the FSMA neglected to include any provisions related to the use of pesticides in the production of the nation's food. Is it not within the realm of possibility that pesticide residues could account for at least some of the "unspecified agents" to which Scallan et al. associate nearly 40 million annual occurrences of foodborne illness?

Pesticide Exposure

Prolonged exposure to pesticides has long been associated with a multitude of chronic human health problems as well as long term damage to the environment and local ecosystems. A 1998 study by Mills found correlations between total pesticide use and certain cancer rates among black and Hispanic males in California. The scope of the study, however, did not include pesticide exposure at the individual level, nor did it account for the dormancy period between exposure and the initial cancer diagnosis. The significance, according to the author, was that many farm workers in the state were traditionally black and Hispanic males, and therefore, those cohorts of the population would be most at risk for long term pesticide exposures.

In perhaps a more alarming study, Bertolote et al. discuss the frequency of suicide via pesticide ingestion in agricultural communities in low- and middle-income countries. Among the implications made by the authors is that "pesticide poisoning is (likely) the most frequently used method of suicide worldwide" (Bertolote et al. 2006). To put this into context, a preferred method of self-inflicted harm in much of the undeveloped world is to ingest the same substances that are used in food production, and

the most recent, sweeping overhaul of food safety laws in one of the world's most developed countries makes little mention of concern about monitoring the continued use of these substances.

Static Toxins

On a global scale, both human and environmental life are exposed to many toxic substances every day. Pesticides, pharmaceuticals, mycotoxins, bacteria, etc. can be introduced to organisms via many naturally occurring avenues. Similar to background radiation, “background” or “static toxins” are not only detected in various foodstuffs, but they are also found (in occasionally elevated traces) in water supplies and air. In 2010, a literature review by Murray et al. compiled data on trace detections of organic chemicals in freshwater environments for comparison to human specific acceptable daily intakes (‘ADIs’). Bifenthrin, cypermethrin, and dieldrin are just a few of the pesticides investigated by Murray et al. which are common to this study. Murray et al. concluded there is an inverse relationship between occurrence data and toxicity data. In other words, occurrence data was not well documented for those compounds with established ADIs, and toxicity data were scarce for those compounds which were most often detected in freshwater environments.

Another study which investigated the occurrence of static toxins was conducted by Harner et al. in 2006. In this pilot study, passive air sampling disks were arranged at “global background sites to test logistical issues associated with a global monitoring network for persistent organic pollutants (POPs).” The findings identified spatial distribution trends of several pesticides, among them are lindane, chlordane, dieldrin and endosulfan as well as some of their primary component compounds. Concentrations in air

were in the picogram per cubic meter range and were occasionally elevated (i.e. 600-800 pg/m³) and varied with latitude and geographic seasonality. Harner et al. made inferences regarding global air streams and currents to partially attribute to the distribution of pollutants.

If research such as that of Harner et al. and Murray et al. demonstrate anything, it is the need for further static pollutant occurrence studies to be conducted more frequently and on a global scale. What these studies indicate is that pesticides and other toxins occur much more frequently than most people might assume, and, in some cases, they are found in surprising concentrations in a seemingly harmless location, like a park. Pesticides are commonly associated with produce, however the fact that humans can get substantial exposures to them by just breathing or drinking water in some locations should be considered a serious public and environmental health concern. Further, if chronic exposure via static toxins is virtually unavoidable, that places more emphasis on the need for the generation of acute exposure data on a large scale.

CHAPTER 3

SAMPLING COMPARISON

While both the PDP and the SCDA randomly sample and screen common agricultural commodities for pesticide residues, the objectives and procedures of each program's sampling method are quite different when examined in detail. Let's begin with an in-depth view of the PDP sampling method. For this research, all available PDP data beginning with calendar year 2001 was collected. While sampling procedures may vary slightly from year to year, PDP's 2011 Annual Summary arbitrarily serves as reference for the initial sampling method overview described in this section.

PDP Sampling Introduction

In 2011, 11 States provided sampling services for the PDP (California, Colorado, Florida, Maryland, Michigan, New York, North Carolina, Ohio, Texas, Washington, and Wisconsin). Collectively, these States represent roughly 50 percent of US population and span all 4 census regions. Additionally, the included states are major sources of domestic produce commodities. The USDA's Agricultural Marketing Service (AMS), working closely with the EPA, carefully select the commodities for sampling to "represent the highest U.S. consumption, with an emphasis on foods consumed by infants and children" (2011 Annual Summary, 1). Unlike State and Federal enforcement programs (such as SCDA), participation as a PDP sampling site is entirely voluntary. In 2011, about 600 sites "granted access and provided information, including site volume

data, to sample collectors. Voluntary cooperation is important to the Pesticide Data Program and makes it possible to adjust sampling protocols in response to fluctuations in food distribution and production” (2011 Annual Summary, 3). “Commodities are cycled through the program approximately every five years. High consumption fresh fruit and vegetable commodities remain in the program for two years” in order to “capture two full growing seasons, thereby capturing any changes due to seasonality or year-to-year variations” (2011 Annual Summary, 1-3).

“Fruit and vegetable samples are collected at terminal markets and large chain store distribution centers from which food commodities are supplied to supermarkets and grocery stores” (2011 Annual Summary, 3). This allows for a wide range detection of residues from crop production applications of pesticides as well as anything that may have been applied post-harvest (such as fungicides, growth regulators, and sprouting inhibitors). This also allows PDP to account for residue degradation during storage of the commodities (2011 Annual Summary, 3).

Pesticides screened in the participating laboratories include those with “current registered uses and compounds for which toxicity data and preliminary estimates of dietary exposure indicate the need for more extensive residue data (2011 Annual Summary, 4). Also monitored are “pesticides for which the EPA has modified use directions (i.e. reduced application rates or frequency) as part of risk management activities (2011 Annual Summary, 4). Additionally, the PDP screens for pesticides which don’t have established domestic tolerance levels, but which are used in other countries that have commodity trade agreements with the U.S. Specific pesticides tested by the PDP can be found in appendices listed at the end of each year’s Annual Summary Report.

PDP Sampling Operations

“The goal of the PDP sampling program is to obtain a statistically defensible representation of the U.S. food supply” with the data reflecting a citizen’s “actual pesticide residue exposure from food” (2011 Annual Summary, 4). The statistical structure and methods of the PDP are meant to “ensure samples are randomly selected from the national food distribution system and reflect what is typically available to the consumer” (2011 Annual Summary, 4).

“In 2011, fruit and vegetables were randomly collected by trained State inspectors at terminal markets and large chain store distribution centers” in the participating States (2011 Annual Summary, 4). Occasionally, when commodities of interest are unavailable at these sites, the samples had to be collected at surrogate or “proxy” sites (i.e. retail markets). Under these circumstances, the commodity would be sampled “in the rear storage area of the retail facility” to rule out any possible consumer contamination as well as to facilitate the inspector’s documentation of necessary sample information from the product boxes. Of the total PDP sampling (which includes egg and milk samples in addition to produce), roughly 34% was collected at proxy sites in calendar year 2011. The most often proxy-collected commodities were baby foods (green beans, pears, and sweet potatoes), canned beets, and canned and frozen spinach (2011 Annual Summary, 4).

Regardless of the sampling site, information regarding the identity and source of the sample is typically available and is “captured at the time of collection for inclusion in the PDP database. A comparison of PDP sample origin data to State production and import data by USDA’s NASS shows PDP sampling is representative of the U.S. food

supply” (2011 Annual Summary, 4). Sampling operations are adjusted to coincide with product availability, and the number of produce samples collected in participating States is determined by State population numbers (2011 Annual Summary, 4).

Sample collectors for the PDP are trained to follow detailed SOPs which give specific conditions and criteria for site selection, sample selection, sample shipping and handling, and chain-of-custody. SOPs are updated as needed and are available to the public via the AMS website (ams.usda.gov). Sample collectors are given Fact Sheets and Quick Reference Guides for use in the field that provide collection details for specific commodities as they are introduced into the program (2011 Annual Summary, 5).

Sample collectors ship samples that are temperature sensitive in “heavy-duty, temperature-controlled containers” and include adequate freezer packs to maintain desired temperatures throughout transit. Temperature controlling parameters are not needed for non-temperature sensitive samples, however such samples are still shipped in “heavy-duty, well-cushioned containers” and, when possible, are shipped on the same day as sample collection to preserve sample integrity. “Non-refrigerated processed commodities (canned beets, baby foods, and canned spinach) are often shipped by ground transportation to reduce shipping costs. Grain samples are collected in pesticide-free polyethylene bags and are shipped in canvas pouches or boxes to the laboratory where the samples are refrigerated pending analysis” (2011 Annual Summary, 6).

“e-SIFs are used for chain-of custody and to capture information needed to characterize the sample” (2011 Annual Summary, 6). Collectors use mobile devices to capture the necessary information which, when combined by computer software, generate a PDP identification number unique to each sample. Any other information available to

the collector regarding each sample is also captured and electronically mailed with the e-SIF the same day as sample collection or, at the very latest, by the next morning so as to ensure that the e-SIF is received by the laboratory prior to the sample itself (2011 Annual Summary, 6).

“Participating State agencies compile and maintain lists of sampling sites. In 2011, approximately 600 sites granted access and provided information, including site volume data, to sample collectors. The States, in turn, provide AMS and NASS with annual volume information for commodities distributed at each site. This information is used to weight the site to determine the probability for sample selection. For example, a weight of 10 may be given to a site that distributes 100,000 pounds of produce annually and a weight of 1 is given to a site that distributes 10,000 pounds. The probability-proportionate-to-size method of site selection then results in the larger site being 10 times more likely to be selected for sampling than the smaller site” (2011 Annual Summary, 6).

“Participating States work with NASS to develop statistical procedures for site weighting and selection. States are also given the option to have NASS perform their quarterly site selection. The number of sampling sites and the volume of produce distributed by the sites vary greatly among the States. Sampling plans that include sampling dates, sites (primary and alternate), targeted commodities, and testing laboratories are prepared by each State on a quarterly basis. Collection of commodities is randomly assigned to weeks of the month, prior to selection of specific sampling dates within a week. Because sampling sites are selected for an entire quarter, States may assign the sites to particular months based on geographic location” (2011 Annual Summary, 6).

“State population figures were used to assign the number of fruit, vegetable, and other specialty samples schedule for collection each month. These population- and distribution-network-based numbers result in the following monthly collection assignments for each State” (See Table 3.1). In 2011, PDP’s monthly sampling target was 62 samples per commodity or 744 samples per commodity annually (2011 Annual Summary, 6).

Table 3.1: PDP Monthly Sample Collection Totals

State	Samples Collected per Commodity per Month
California	13
Colorado	2
Florida	7
Maryland	4
Michigan	6
New York	9
Ohio	6
Texas	9
Washington	4
Wisconsin	2
Total	62

SCDA Sampling Introduction

Under the South Carolina Department of Agriculture’s mission statement, the agency aims to “promote and nurture the growth and development of South Carolina's

agriculture industry and its related businesses while ensuring the safety and security of the buying public” (South Carolina Department of Agriculture; “Our Mission”).

As part of the agency’s mission to ensure the safety of the buying public, the SCDA operates a Consumer Protection Division, which includes a Laboratory Services department. The laboratory is divided into four sections – Chemical Residue, Food & Feed, Petroleum, and Seed – each of which is responsible for checking behind manufacturer labeling to ensure the consumer is getting what they pay for in a given commodity. For example, the petroleum lab might test a sample of gasoline advertised as “Premium without ethanol” to ensure that the octane rating is accurate and to confirm that ethanol is not present. Additionally, the petroleum lab would also test for the presence of water and/or sediment in the gas sample to ensure that nothing other than the advertised gasoline is coming through the line at that particular pump. The lab’s analytical test results allow the SCDA to act as a regulatory authority and, as such, levy fines, issue stop-sales, or shut down entire stores.

A significant part of the lab’s sample load comes directly from concerned consumers, who may request laboratory analyses on their submitted samples free of charge as long as they reside in, and pay taxes to, the state of South Carolina. Results on submitted samples are considered as “for information only.” The bulk of the laboratory’s workload is collected and either shipped or hand-delivered to the lab by any of the agency’s 20 official inspectors. If a consumer wants a marketed commodity tested, he/she must file a complaint which will prompt official sample collection by an agency inspector. A sample is only considered “official” if the sample is collected by an agency

inspector and chain-of-custody is maintained throughout the sample's transit to the laboratory. The agency can take regulatory action only on official samples.

Sampling Procedures

In stark contrast to the rigidity of PDP sampling guidelines, SCDA inspectors follow a much less rigorous structure. In a typical workweek, the chemical residue laboratory receives 20 official samples. The lab also occasionally receives submitted samples directly from consumers and participates in a soil testing program for pesticide residues. Adjustments are made accordingly when the lab is short-staffed as there are only two analysts.

As stated previously, SCDA's Consumer Protection Division staffs 20 official inspectors. Most inspectors cover two to three counties (or portions thereof), or as little as one county in the state's more densely populated regions. In largely rural parts of the state, an inspector may cover up to 5 counties. For sample collection, inspectors are assigned, on a weekly basis, which lab to pull samples for. According to Consumer Protection administrative staff, who assign the sample collection duties weekly, the inspectors are assigned produce sampling once every four to five weeks, or roughly once per month. Unlike PDP sampling guidelines, SCDA's inspectors have a great deal of liberty in choosing from where to collect their samples, what commodities to sample, and how much sample to collect.

Whereas the PDP samples from distribution centers (closer to commodity origin), SCDA samples from retail stores (closer to commodity consumption). The PDP's sampling sites are predetermined while SCDA's are randomly chosen entirely by the inspector. In choosing from which store to collect samples, a SCDA inspector often

selects from any of the locations he/she already plans to be visiting during the workweek. Other job duties of SCDA inspectors include checking the accuracy of all scales used at points of sale within their assigned territories. It is this particular job duty that typically defines from where an inspector is going to sample produce. When an inspector is assigned sampling for the Chemical Residue lab, they usually sample from whichever store(s) they had already planned to be working at during that particular week (checking scale accuracy). There is no managerial guidance which dictates from which store they should sample. Other than the criteria that the store be located within their territory, the sampling location is entirely at the inspector's discretion.

Also at the discretion of the inspector is the choice of which commodities to sample. You may recall that PDP's sample collectors are told specifically which fruits, vegetables, or canned goods are to be collected. By contrast, SCDA's inspectors are at liberty to choose from any of the produce options available at their sampling site. Their only restrictions are: (1) to not sample onions (due to matrix complications which result in poor data), and (2) to only sparingly sample berries (simply because in recent years, commodities such as strawberries, blackberries, and raspberries were sampled too often). Inspectors are asked to collect at least 16 ounces per sample and must collect from the front of the store where the commodities are available to consumers. Inspectors should only be entering storage areas in the back of the store if they need to collect any additional information pertaining to a commodity's origin or identity. Samples are then paid for (at the store's posted rate) with a department-issued credit card.

After collection, samples are transported to the SCDA Consumer Protection Lab for pesticide residue analysis. Sample integrity is maintained via thermo-insulated

shipping boxes complete with freezer packs. Inspectors working local to the lab usually hand deliver their samples within 24 hours. Those working farther away transport their samples to county collection points where they are picked up daily by a state-sponsored inter-agency courier. Samples usually arrive to the laboratory one day after collection, but may also arrive as quickly as the same day, or as late as two days after collection in rare cases. Table 3.2 on the following page displays a summary of the major differences between PDP and SCDA sampling operations and program objectives.

Sampling Bias

The liberty that sample collectors are given in the market basket survey allows for a source of selection bias which is not inherently present in the PDP's sampling method. For example, an inspector might be more likely to sample from a batch of apples if the apples either appear exceptionally fresh or exceptionally rotten. Perhaps if a selection of produce looks somewhat tainted to the naked eye, a market basket collector may assume there is a higher probability that the commodity contains elevated levels of pesticide residues. Alternatively, if a batch of a given commodity appeals as visually appetizing to an inspector, then maybe he or she inherently feels less of a need to sample said commodity as it is less likely to contain detectable levels of residues. However, the question of – “Who would intentionally purchase and eat food that is visibly rotten or which is otherwise visually undesirable?” – should be kept in mind. If the market basket survey were intended simply to detect as many chemical residues as possible on all food regardless of appearance, then of course a selection bias would play a significant role in an inspector's choice of commodities to sample. However, because the goal of the market basket survey is consumer protection as per the SCDA's mission statement, then

Table 3.2: Summary of Major Sampling Method Differences

	PDP	SCDA
Program Goal(s):	<ul style="list-style-type: none"> • Obtain data about nation’s food supply. • Establish tolerance limits for new pesticides. 	<ul style="list-style-type: none"> • Help ensure safety of the consumer.
Sampling Sites:	<ul style="list-style-type: none"> • Volunteering terminal markets & distribution centers. • Retail stores – alternate sites. 	<ul style="list-style-type: none"> • Retail stores at inspectors’ discretion within assigned territories.
Food Supply Position:	<ul style="list-style-type: none"> • Sampled closer to point of origin. 	<ul style="list-style-type: none"> • Sampled at point of sale.
Transport to Lab:	<ul style="list-style-type: none"> • Shipped in thermally insulated containers. • Arrival time – 1 day. 	<ul style="list-style-type: none"> • Shipped or hand delivered in thermally insulated containers. • Arrival time ~ 1 day or less.
Commodities Sampled:	<ul style="list-style-type: none"> • Determined annually by AMS & EPA. • Emphasis given to foods consumed by infants and newborns. 	<ul style="list-style-type: none"> • At inspector’s discretion with little instruction.

inspectors should be sampling foods that are likely to be purchased by the typical consumer (i.e. the “cleanest” appearing commodities available). Therefore, if commodity appearance is indicative of pesticide contamination, then any selection bias that exists the market basket method is likely biased towards the most visually appealing foodstuffs (against likely detections of residues). How much this source of bias might influence outcomes in the market basket survey remains to be seen and is likely undeterminable by the scope of this study.

CHAPTER 4

MATERIALS AND METHODS

For this research, PDP annual summary reports for calendar years 2001-2014 (most recent) were collected. Each year's report begins with a detailed introduction describing which commodities were chosen for sampling that year, which states were participating in the PDP that year, as well as information on how participating state population figures were used to determine the number of samples to be collected. The introduction also describes the sample collection and transport processes, shipping to participating laboratories, and laboratory analytical methodology. Following the introduction are datasets in multiple, but somewhat redundant formats. First the data is sorted by chemical compound detected and lists all the commodities in which each compound was detected along with the relevant descriptive statistics which are described below. Following, the data is then sorted by commodity and lists each compound detected specific to each commodity along with similar descriptive statistics. Listed in all datasets are:

- (1) The number of times a compound was detected specific to commodity.
- (2) The total number of samples.
- (3) A range of LOD (lowest detection – highest detection).
- (4) EPA established tolerance (if any).

Beyond the primary dataset, the PDP Annual Summary also contains appendices which separate the year's data by country of origin, sort detections by organic vs. non-organic

product labels, and present special studies results such as residue analyses on water, soil, meat, and fish.

A digital database containing the entire PDP history was also obtained. The user-friendly interface of the PDP Search Utility enables searching by compound or commodity (or combination thereof) and allows for several different results displays. Due to its ease of historical searching, the digital PDP Search Utility was used most often to find data, while the hardcopy summary reports were used as reference or to find additional info as needed.

For comparison to the PDP datasets, Annual Reports from the SCDA's Chemical Residue Lab beginning with fiscal year 2001-02 have been gathered. This brings about a major assumption that needs to be addressed before going forward: Because the annual reports of interest are somewhat staggered with respect to time, it will be necessary to assume that SCDA fiscal year 2001-02 corresponds with PDP calendar year 2001, and so forth. From this point forward, any SCDA fiscal year will be referred to by its leading calendar year date.

The SCDA annual report begins with a brief summary of the major findings over the year and the summary data then follows in spreadsheet format. Data is sorted alphabetically by chemical compound. Listed for each compound are:

- (1) any commodities for which detections were made.
- (2) a range of LOD specific to the commodity.
- (3) EPA tolerance (if any).

After the summary data, there is a small table containing any compounds which were detected in 'over-tolerance' levels along with the respective commodity(-ies) the

compound was found in, the detected concentration(s), and the listed EPA tolerance(s), if any. Detections of compounds without an established tolerance level are also found in this table.

The data contained within both databases are presented in nearly an identical fashion with respect to the number of detections of a compound within a commodity as well as the range of detected concentrations. The following table illustrates how the data are presented in each of the annual reports of these two residue monitoring programs (using hypothetical data and EPA tolerances).

Table 4.1: Example of Surveys' Annual Data.

SCDA				
Residue	Matrix	Frequency	Range (ppm)	Tolerance (ppm)
Acephate	Strawberries	6	0.07 – 0.15	0.2
	Tomatoes	3	0.10 – 0.19	1.0

PDP				
Residue	Matrix	Frequency	Range (ppm)	Tolerance (ppm)
Acephate	Onions	40/700	0.50 – 2.50	5.0
	Tomatoes	23/550	0.06 – 0.27	1.0

The information contained within the respective databases is suitable for comparing the detected concentrations between the two surveys of all compounds for which there were any detections. For example, in the table above, acephate was detected in tomatoes across both surveys. Therefore, the detected concentrations are paired for comparison. If the SCDA data yields similar detected concentrations when compared to PDP, that would be indicative of an effective market-basket survey. Notice, however, that the same compound was detected in onions in the PDP, but not by the SCDA. Therefore, if it can be determined through an historical record search that onions were sampled

during the fiscal year of interest, then a detection of zero can be assigned for that particular compound in onions. Such a finding would not necessarily be indicative of an ineffective market-basket survey, but should be noted nonetheless.

The SCDA annual reports do not indicate the total number of times each commodity was sampled. All that is listed is how many times a particular residue was detected in a given commodity. For example, from the table on the previous page, acephate was detected 6 times in strawberries. What is not shown is how many times strawberries were sampled and analyzed that year. For example, using the same hypothetical table above, PDP data indicates acephate was found 23 times in 550 samples, or roughly in 4.2% of all tomatoes sampled. SCDA data however only indicates the total number of detections of acephate in tomatoes (3). Also listed in the PDP databases, and not in SCDA reports, are compounds' mean detected concentrations. It should be noted, however, that non-detects are not weighted in a compound's mean detection. For example, again using the table above, the mean would be interpreted as: "Acephate was detected in 4.2% of tomatoes at a mean of 0.1 ppm." The digital PDP Search Utility, provided individual detected concentrations for use in calculating standard deviations when necessary.

Fortunately, several years of SCDA archived paperwork were available in storage. The archived information was researched for total sample counts and separated by commodities of interest to the relevant year. From the total counts obtained by the paperwork and the number of detections in the annual report, a detection rate was then calculated. Corresponding laboratory identification numbers from the archived paperwork were used to find detection data which allowed for mean and standard

deviation calculations. Unfortunately, the archived paperwork only dates from year 2014 to year 2009. As such, neither SCDA detection frequencies nor mean detections could be obtained for the earlier years and, therefore, data from years 2001 through 2008 were discarded from this study.

Database Filtering

Considering the volume of data available in each database, the numbers of years of interest, and the differences between the two databases with respect to commodities sampled and analyzed, the data must be filtered in some manner. The process of comparing these databases provides for the data to filter itself.

Recall that the PDP surveys predetermined commodities while the SCDA samples potentially any commodity available for consumer purchase. The logical approach, therefore, is to filter the SCDA summary reports by detections on commodities which were also sampled by the PDP. Table 4.2 on the following page illustrates this approach to database filtering using the commodities sampled by PDP in 2011.

Therefore, all detections from the commodities common to both databases are matched for comparison. Where applicable, SCDA's archives were searched to separate data by commodity variety (For example, SCDA Annual Report only lists detections in "peppers"). To get the most accurate pairing, archived paperwork was searched for sample identification information in order to separate detections in "hot peppers" from those in "bell peppers." This study will only focus on positive detections and therefore the unmatched PDP commodities (Cabbage, Cantaloupe, etc.) were discarded.

Table 4.2: Commodity Filtering Approach

PDP Sampled Commodities:	
Cabbage	Onions
Cantaloupe	Papaya
Cauliflower	Plums
Cherry Tomatoes	Snap Peas
Hot Peppers	Sweet Bell Peppers
Lettuce	Tangerines
Mushrooms	Winter Squash
Of the above, SCDA detected residues on:	
Lettuce	Snap Peas
Mushrooms	Squash
Peppers	Tomatoes
Plums	

After matching the commodities in which detections were made across both surveys, the remaining data was filtered according to which compounds were detected. SCDA’s lab only screens for just over 120 chemical compounds, while the PDP screens for upwards of 500 compounds. In addition, certain residues are metabolites of parent pesticides. Therefore, only detected concentrations of identical compounds or their metabolites were paired for analysis. This second step filtered the data further. Table 4.3 on page 27 illustrates this second approach to filtering using hypothetical compounds detected in samples of apples as an example.

Therefore, any compounds which were detected by the PDP, but were not screened for by SCDA were discarded. Now, each year’s data has been filtered twice – first with respect to commodity and again with respect to chemical compound. This leaves a significantly smaller dataset to work with for each year of interest.

Table 4.3: Compound Filtering Approach

Compound	Residue Detections in Apples in 2011:		Accept/Discard
	PDP detections?	In SCDA screen?	
X	Yes	Yes	Accept
Y	Yes	No	Discard
Z (parent of A)	Yes	No	Accept
A (metabolite of Z)	No	Yes	(Conditionally)

Linear Regression Modeling

If the hypothesis that these two databases yield similar results is true, then the outcome of one method could predict the outcome of the other. Therefore, this tool is the most obvious and logical approach with which to begin comparing the datasets.

Regression models were constructed from the mean detected concentrations of matching compounds in each commodity, per each year and over all years of interest to the study.

In all regression models, SCDA values serve as the dependent variable.

Additionally, compound detection frequencies were paired and plotted in a similar manner as described above. Regression models were made for each of the following:

- (1) Detection frequencies per commodity.
- (2) Overall detection frequencies per year.

This approach paints a broad picture of the overall efficacy of the market-basket survey as compared to the robust PDP program design as an attempt to answer the question “How *often* does the SCDA method detect the same compounds as the PDP?”

T-Test

Another statistical tool of interest to this study is the Student’s T-test. This was used to investigate whether SCDA’s mean detected concentration for a given chemical

compound found in a given commodity differs significantly from the analogous PDP value. For example, let PDP's mean detected concentration of acephate found in apples = \bar{Y}_0 and let SCDA's mean detected concentration of acephate found in apples = \bar{Y}_1 . The t-test investigates whether the two mean detected concentrations differ significantly from each other.

Data Pairing and SAS

Microsoft Excel was used to construct a tabular format of the paired data for all years of interest. Where applicable and necessary, a separate spreadsheet was also used for calculating means and standard deviations for certain compound/matrix detections. After data pairing was completed, most of the values were transferred to a new spreadsheet and resorted for upload to Statistical Analysis System (SAS) University Edition Online Studio. A period symbol was used and inserted for any missing values.

SAS was used to sort, group, and analyze the multivariate data. The software's "proc reg" and "proc ttest" function codes were used to obtain linear regression models and t-test results, respectively. Microsoft Excel was used again to tabulate and summarize the SAS result output.

CHAPTER 5

RESULTS

The SAS output for simple linear regression models contains an abundance of information. As such, it would be impractical to list all the data associated with each regression model output. Recall that a primary goal of this study is to ascertain whether the outcome of one survey can predict the outcome of the other. For each regression model, PDP data serves as the predictor (X axis) and SCDA data is the response, or dependent, variable (Y axis). The following data, parameter estimates and measures of fit will be presented in tabular form for each regression model:

- (1) n – the number of observations used to make each model.
- (2) Y-int – the height of the regression line when it crosses the Y axis (with error).
- (3) Slope – an estimate of the amount of increase in the SCDA data for each 1 unit increase in the PDP data (with error).
- (4) r^2 – the proportion of total variance in the SCDA data explained by the regression on the analogous PDP data.
- (5) Root MSE – the standard deviation of the error between observed values and the regression model. Low Root MSE indicates a better model fit to the individual observations.

As with the linear regression models, a SAS t-test result output also contains a wealth of information. Each t-test examines whether the two surveys' means differ significantly from each other when considering certain conditions. The common

significance level of $\alpha = 0.05$ (or 5% significance) was pre-determined for each t-test. Thus, there is 95% confidence in each t-test, and the study assumes a 5% chance of wrongly concluding that two tested means differ significantly (a Type I error). The following data will be listed for each t-test:

- (1) n – the number of observations (the number of different compounds with paired detection means).
- (2) t – the computed test statistic.
- (3) p -value – the probability of observing a greater absolute value of t if the two means don't differ significantly.

Finally, when observing the results of these analyses, it is important to remember that this is a longitudinal, broad based, multi-condition study, and in many cases, one or more parameters must be removed from the result display at a time. For example, in the following Table 5.1, linear regression results per individual matrix (commodity) are displayed. Neither the detected compounds nor their associated detection means are shown. Therefore, these results are presented as “Compound-Removed.” To interpret the data, consider the first row in table 5.1. There were eight different compounds detected in apples in 2009 by both surveys. Recall that a PDP mean might represent tens to hundreds of detections while the analogous sample size for SCDA is usually 10 or less. Each data point represents one PDP mean detection (X-axis) and one SCDA mean detection (Y-axis). Models were only made when the number of observations was greater than two.

On the surface, the results in Table 5.1 seem to represent more coincidence as they don't appear to follow a pattern. 61% of the generally positive slopes are also greater than one. Therefore, for a one-unit increase in a PDP mean, 61% of the models predict

greater than one-unit increase in a SCDA mean. This is likely accounted for by extreme observations in low sampling counts which certainly influence each SCDA mean. Nearly half (11 of 23) of the models have correlation coefficients greater than 0.50 and there seems to be more occurrences of better correlation in years 2009-2011. The number of observations per plot also seems not to be associated with better correlation between the two means. Just five of 12 models with $n \geq 5$ also had $r^2 \geq 0.9$.

Table 5.1: Regression of Mean Detections by Matrix (Compound-Removed)

Year	Matrix	n	Y-int (error)	Slope (error)	r^2	Root MSE
2009	Apple	8	0.03 (0.04)	3.06 (0.20)	0.97	0.0841
	Grape	3	-0.28 (1.46)	16.25 (13.42)	0.59	1.5344
	Pear	4	0.08 (0.03)	-0.23 (0.17)	0.48	0.0426
	Spinach	3	0.90 (0.99)	1.09 (0.66)	0.73	1.1058
	Strawberry	5	0.04 (0.13)	3.45 (0.39)	0.96	0.2413
2010	Apple	4	-0.08 (0.23)	1.33 (0.86)	0.55	0.2947
	Bell Pepper	4	-0.13 (0.16)	4.88 (2.35)	0.68	0.1569
2011	Bell Pepper	5	0.06 (0.04)	-0.11 (0.69)	0.01	0.0542
	Snap Pea	3	-0.04 (0.04)	1.46 (0.11)	0.99	0.0490
2012	Bell Pepper	4	0.14 (0.05)	-0.31 (1.04)	0.04	0.0562
2013	Bean	5	0.05 (0.01)	-0.36 (0.32)	0.29	0.0232
	Peach	8	0.08 (0.08)	2.14 (0.02)	0.96	0.1658
	Raspberry	5	0.10 (0.04)	0.76 (0.12)	0.94	0.0638
	Squash	4	0.02 (0.01)	0.27 (0.47)	0.14	0.0170
2014	Apple	5	0.03 (0.75)	3.60 (3.27)	0.29	0.8861
	Bean	5	0.02 (0.06)	1.01 (0.28)	0.81	0.0862
	Blueberry	9	-0.21 (0.51)	4.24 (3.87)	0.15	0.5702
	Broccoli	4	0.23 (0.15)	-0.54 (0.82)	0.18	0.2187
	Celery	4	0.28 (2.13)	9.08 (24.31)	0.07	1.7186
	Peach	7	0.34 (0.18)	0.61 (0.53)	0.21	0.3357
	Squash	3	0.23 (0.21)	-3.43 (4.70)	0.35	0.1016
	Strawberry	10	0.03 (0.04)	1.72 (0.14)	0.95	0.1139
Tomato	6	0.17 (0.29)	2.12 (10.72)	0.01	0.3610	

The regression models in Table 5.1 are complemented by t-tests of the same data pairings, the results of which are displayed in the next table.

Table 5.2: T-test by Matrix (Compound-Removed)

Year	Matrix	n	t	p-value
2009	Apple	8	2.44	0.0448
	Cucumber	2	3.00	0.2048
	Grape	3	1.10	0.3847
	Pear	4	-0.83	0.4685
	Spinach	3	2.20	0.1593
	Strawberry	5	1.46	0.2191
2010	Apple	4	-0.10	0.9264
	Bell Pepper	4	0.96	0.4061
	Cucumber	2	-1.00	0.5000
2011	Bell Pepper	5	0.07	0.9478
	Lettuce	2	1.02	0.4933
	Mushroom	2	1.33	0.4097
	Snap Pea	3	0.87	0.4771
2012	Bell Pepper	4	2.77	0.0696
	Mushroom	2	1.14	0.4576
	Plum	2	-0.84	0.5570
2013	Bean	5	0.51	0.6370
	Mushroom	2	0.89	0.5385
	Peach	8	2.63	0.0340
	Raspberry	5	1.45	0.2200
	Squash	4	0.24	0.8240
2014	Apple	5	1.43	0.2261
	Bean	5	0.54	0.6183
	Blueberry	9	0.96	0.3654
	Broccoli	4	0.30	0.7811
	Celery	4	1.28	0.2906
	Nectarine	2	0.89	0.5353
	Peach	7	2.00	0.0923
	Squash	3	0.64	0.5857
	Strawberry	10	2.35	0.0436
	Tomatoes	6	1.45	0.2062

Unlike the corresponding regression models, t-tests were computed for $n = 2$ observations and included in the resulting dataset. At the $\alpha = 0.05$ significance level, 90% of all t-tests do not detect a difference in the true mean detection of a given residue between the two surveys. There are only three instances of a t-test offering sufficient evidence to reject the hypothesis that the means don't differ. Those three instances occur in the four datasets with the largest number of observations. The following table summarizes Tables 5.1 and 5.2 across all years when the number of observations was greater than seven in compound-removed results.

Table 5.3: Regression/T-test Summary for Large n (Compound-Removed)

Year	Matrix	n	t	p-value	Y-int	(err)	Slope	(err)	r^2	RMSE
2009	Apple	8	2.44	0.04	0.03	(.04)	3.06	(0.20)	.97	0.08
2013	Peach	8	2.63	0.03	0.08	(.08)	2.14	(0.02)	.96	0.17
2014	Blueberry	9	0.96	0.37	-0.21	(.51)	4.24	(3.87)	.15	0.57
	Strawberry	10	2.35	0.04	0.03	(.04)	1.72	(0.14)	.95	0.11

Table 5.3 is strong evidence of a difference between the long run mean outcomes of the sampling surveys. The t-tests provide enough evidence that the true means do in fact differ, while the positive, greater than one pattern displayed by the slopes predicts a greater increase in a SCDA mean detection per one unit increase in a PDP mean. Due to the differences in food supply sampling locations created by each survey, it's reasonable to assume that both – (1) residues on SCDA samples should be smaller on average than in PDP sampling since the residues have longer to volatilize, and (2) there are sufficient chances of further contamination before the commodities reach store shelves which would suggest that the average detection is larger in the SCDA market-basket method.

A more comprehensive compound-removed result dataset is obtained by a t-test of detection means over all matrices with no temporal dimension as shown in the next table (Table 5.4). While thorough, the data are not particularly indicative of anything new. At the $\alpha = 0.05$ significance level, there is sufficient evidence of differing detection means within the same 3 commodities as previously described in Table 5.3 (apples, peaches, and strawberries).

Table 5.4: Cumulative T-test by Matrix (Compound-Removed)

Matrix	n	t	p-value
Apple	17	2.26	0.0383
Bean	10	0.78	0.4565
Bell Pepper	13	1.71	0.1131
Blueberry	9	0.96	0.3654
Broccoli	4	0.30	0.7811
Celery	5	1.29	0.2657
Cucumber	4	-0.19	0.8614
Grape	3	1.10	0.3847
Lettuce	3	1.03	0.4106
Mushroom	6	2.03	0.0980
Nectarine	3	0.92	0.4556
Peach	15	3.34	0.0048
Pear	5	-0.42	0.6972
Plum	4	0.47	0.6731
Raspberry	5	1.45	0.2200
Snap Pea	3	0.87	0.4771
Spinach	3	2.20	0.1593
Squash	8	0.87	0.4140
Strawberry	15	2.25	0.0412
Sweet Potato	2	3.60	0.1725
Tomato	6	1.45	0.2062

Table 5.5 on the following page shows the regression model outputs of paired detection rates. To interpret these results, each data point represents the frequency of

which a compound was detected in all samples of a given matrix. For example, in 2010 SCDA detected the residue dicloran in 33% of sampled sweet potatoes. PDP detected the same residue in 46% of their sampled sweet potatoes (There is no regression model for sweet potatoes, however as dicloran was the only observation that year, which is somewhat remarkable on its own).

Table 5.5: Regression of Detection Frequencies (Compound/Mean-Removed)

Year	Matrix	n	Y-int. (error)	Slope (error)	r ²	Root MSE
2009	Apple	8	8.28 (6.56)	0.10 (0.17)	0.06	13.9277
	Grape	3	26.81 (5.47)	-0.52 (0.55)	0.47	7.6730
	Pear	4	10.84 (2.73)	-0.33 (0.35)	0.31	3.6462
	Spinach	3	-8.59 (11.00)	1.07 (0.34)	0.91	11.0128
	Strawberry	5	-11.89 (12.56)	1.68 (0.52)	0.78	16.3650
2010	Apple	4	1.25 (13.30)	0.22 (0.23)	0.32	16.4995
2011	Bell Pepper	5	7.20 (0.61)	-0.20 (0.06)	0.77	0.7774
2012	Bell Pepper	4	1.76 (2.68)	0.70 (0.22)	0.83	3.0748
2013	Bean	5	3.03 (2.92)	0.80 (0.47)	0.50	5.0726
	Peach	8	5.03 (2.18)	0.17 (0.06)	0.55	3.9245
	Raspberry	5	4.02 (6.06)	0.72 (0.41)	0.50	7.4422
2014	Apple	5	9.22 (12.48)	0.33 (0.34)	0.24	16.6007
	Bean	5	16.70 (13.44)	-0.31 (1.18)	0.02	17.3977
	Blueberry	9	4.79 (4.61)	0.64 (0.23)	0.52	8.1824
	Celery	4	5.99 (5.06)	0.03 (0.17)	0.02	3.3647
	Peach	7	19.26 (4.94)	-0.23 (0.17)	0.27	8.7564
	Squash	3	6.88 (5.31)	0.24 (1.14)	0.04	5.3320
	Strawberry	10	1.79 (6.51)	0.32 (0.17)	0.31	11.8515
	Tomato	6	1.66 (1.43)	0.20 (0.17)	0.27	2.1697

As seen in an earlier dataset of compound-removed regression models, the squared correlation coefficients in Table 5.5 in general are greater than 0.5 initially, and then correlations appear to fall off with increasing year. Data points in this regression set were further restricted as the SCDA data might have multiple detections in one sample

per matrix for the entire year. Such an instance leads to identical values of y plotted against varying values of x . For example, in 2014, bifenthrin, boscalid, cypermethrin and permethrin were each detected once out of 15 samples of broccoli for a frequency of 6.67% each. PDP found the same compounds in 0.7%, 1.83%, 1.12%, and 1.4%, respectively, of all broccoli sampled in 2014. Such a dataset when plotted yields a horizontal line through $y=6.67$ with a slope of zero.

63% of the slopes in Table 5.5 are between zero and one which predicts that most SCDA detection frequencies increase by only a fraction per one-unit of increase in corresponding PDP frequencies. This observation is somewhat expected due to differences in the surveys' sampling volumes alone. However, like extrema effects on means of small sample sizes, a SCDA detection frequency can be easily skewed for those lesser sampled commodities (i.e. a compound detected once in only two samples yields 50% detection rate of the compound in the matrix).

Perhaps a more informative approach in analyzing detection rates is to examine which compounds were repeatedly detected in the same matrix longitudinally over multiple years. Such an approach is illustrated in Table 5.6 on the next page. For example, the residues diphenylamine (DPA) and thiabendazole were each detected in apples in both surveys in 2009, 2010, and 2014 (apples were not sampled by PDP in years 2011-2013). After filtering the complete dataset for compounds which were detected in the same matrix more than twice over the entire time frame, only six such instances were found. To interpret this data, SCDA detected thiabendazole in apples in frequencies of 4.3% (2009), 2.4% (2010), and 10.5% (2014). The PDP's detection frequencies were 75.4%, 80.8%, 48.6%, respectively.

From these results, two assumptions can reasonably be made. First, thiabendazole is a compound that is frequently applied on apples. There's clear evidence across a six-year time frame to support a frequent association of the compound with the commodity. Secondly, this compound's residue diminishes significantly during transport between PDP sampling sites and retail store shelves. Reasons to support this finding are unknown. Inherent characteristics of matrices and compounds will be briefly examined a little later. The data for dieldrin found in squash follow a similar regression model as thiabendazole in apples, though that data would suggest that dieldrin's detection frequency in squash decreases by three units per one-unit increase in PDP detection frequency.

Table 5.6: Regression of Detection Frequencies by Matrix-Compound (Year-Removed)

Matrix	Compound	n	Y-int	(error)	Slope	(error)	r ²	Root MSE
Apple	DPA	3	40.14	(33.95)	-0.09	(0.46)	0.04	6.9421
	Thiabendazole	3	22.58	(1.13)	-0.25	(0.02)	1.00	0.3947
Bell Pepper	Cyhalothrin	3	7.71	(4.52)	-0.52	(0.80)	0.30	1.4999
Mushroom	Chlorothalonil	3	10.94	(6.17)	-25.39	(46.42)	0.23	6.3764
Plum	Iprodione	3	13.91	(52.25)	1.07	(1.40)	0.37	52.4817
Squash	Dieldrin	3	12.12	(0.90)	-3.08	(0.38)	0.98	0.7234

To complement these regression models, paired t-tests of the detection means were again computed for the same conditions and are displayed in the following Table 5.7. All t-tests support the hypothesis that the mean detections do not differ significantly for alpha = 0.05. Recall that the opposite result was determined for apples in prior t-tests when compounds were removed as a test parameter. Tables 5.6 and 5.7 are more strong evidence to support (1) the effectiveness of the market-basket survey, and (2) the

similarities in survey outcomes (especially for those commodities which are sampled most often).

Table 5.7: T-Tests of Longitudinal Detection Means

Matrix	Compound	n	t	p-value
Apple	DPA	3	1.92	0.1942
	Thiabendazole	3	1.09	0.3885
Bell Pepper	Cyhalothrin	3	0.00	1.0000
Mushroom	Chlorothalonil	3	0.65	0.5799
Plum	Iprodione	3	0.41	0.7225
Squash	Dieldrin	3	-0.46	0.6914

In a longitudinal look at detection means by chemical compound (matrix-removed), other inferences can be made (see Table 5.8 on the following page). To interpret the data, consider captan detections in 2009. Each survey had a mean detection of captan occurring in four different matrices, whether it was detected just once or many times throughout the sampling period (For reference, 2009 saw 13 overall matching commodities between the surveys, eight of which had matching detections). There is just one occurrence of a p-value low enough to conclude differing detection means (cyfluthrin – 2009) though 3 others come close (malthion – 2009, cyhalothrin – 2012, and cypermethrin – 2013).

The data when presented in this fashion give some idea of the distribution and overall variety of compounds throughout the population of all commodities and is somewhat indicative of indiscriminant usage of many pesticides in application processes. For example, revisit Table 5.2 on page 31. In 2009, there were eight different compounds detected by both surveys in apples, five paired detections in strawberries and four in

Table 5.8: T-test by Compound (Matrix-Removed)

Year	Compound	n	t	p-value
2009	Azinphos Methyl	2	0.67	0.6257
	Captan	4	0.90	0.4366
	Cyfluthrin	2	18.00	0.0353
	Malathion	2	8.33	0.0760
	Phosmet	2	0.41	0.7537
	Thiabendazole	2	3.10	0.1989
2010	Bifenthrin	2	0.00	1.0000
	Dursban	3	0.85	0.4846
2011	Cyhalothrin	2	-0.33	0.7952
	Cypermethrin	2	-5.00	0.1257
	Iprodione	2	1.27	0.4240
	Permethrin	3	1.45	0.2832
2012	Boscalid	2	1.25	0.4296
	Cyhalothrin	2	7.00	0.0903
2013	Boscalid	4	0.62	0.5791
	Captan	2	0.71	0.6051
	Cyhalothrin	2	1.80	0.3228
	Cypermethrin	2	11.00	0.0577
	Esfenvalerate	2	1.00	0.5000
	Iprodione	3	1.93	0.1930
	Malathion	2	4.20	0.1488
2014	Acephate	2	0.96	0.5145
	Bifenthrin	7	0.83	0.4362
	Boscalid	8	1.35	0.2190
	Chlorothalonil	3	0.51	0.6613
	Cypermethrin	4	-1.24	0.3039
	Cyprodinil	3	1.61	0.2479
	Fludioxinil	5	2.02	0.1132
	Iprodione	2	2.45	0.2465
	Malathion	3	2.05	0.1770
	Myclobutanil	3	2.51	0.1286
	Phosmet	3	0.12	0.9172
	Propicanazole	2	1.29	0.4190

pears. As Table 5.8 shows, there were only six compounds found in at least two matrices that year (azinphos methyl, captan, cyfluthrin, malathion, phosmet, and thiabendazole).

Presumably, if evidence suggests that two chemical compounds which are applied to apples during harvest are not also applied to other commodities, then the need for the other six compounds in treating apples is questionable. Alternatively, 2014 results indicate 12 compounds were detected in multiple matrices (there were only 11 different commodities sampled that year). Table 5.9 below filters the preceding table for t-test results when the number of observations was greater than two.

Table 5.9: T-tests by Compound for $n > 2$ (Matrix Removed)

Year	Compound	n	t	p-value
2009	Captan	4	0.90	0.4366
2010	Dursban	3	0.85	0.4846
2011	Permethrin	3	1.45	0.2832
2013	Boscalid	4	0.62	0.5791
	Iprodione	3	1.93	0.1930
2014	Bifenthrin	7	0.83	0.4362
	Boscalid	8	1.35	0.2190
	Chlorothalonil	3	0.51	0.6613
	Cypermethrin	4	-1.24	0.3039
	Cyprodinil	3	1.61	0.2479
	Fludioxinil	5	2.02	0.1132
	Malathion	3	2.05	0.1770
	Myclobutanil	3	2.51	0.1286
	Phosmet	3	0.12	0.9172

Finally, a cumulative look at the t-test by compound result dataset is shown in Table 5.10 on the next page.

Table 5.10: Cumulative T-test by Compound (Matrix/Year-Removed)

Compound	n	t	p-value
Acephate	2	0.96	0.5145
Azinphos Methyl	3	0.30	0.7892
Bifenthrin	12	0.54	0.5993
Boscalid	15	1.73	0.1061
Captan	9	1.41	0.1960
Chlorothalonil	6	0.74	0.4911
Cyfluthrin	5	2.49	0.0674
Cyhalothrin	8	1.64	0.1443
Cypermethrin	10	0.75	0.4696
Cyprodinil	3	1.61	0.2479
Dicloran	3	1.19	0.3573
Dieldrin	4	-0.23	0.8361
DPA	3	1.92	0.1942
Dursban	6	0.98	0.3700
Esfenvalerate	4	2.23	0.1115
Fludioxonil	6	2.54	0.0519
Iprodione	9	2.23	0.0565
Malathion	7	5.10	0.0022
Myclobutanil	5	2.53	0.0650
Permethrin	5	2.62	0.0589
Phosmet	8	1.14	0.2901
Propiconazole	4	1.73	0.1817
Thiabendazole	6	2.48	0.0557

As observed in Table 5.8, most of the data is not supporting evidence of significantly different detection means. At the $\alpha = 0.5$ significance level, just one of the 23 different compounds with matching detections over six years of paired data shows evidence of a significantly different detection mean from one survey to the next. On a broad scale, this is evidence (1) to further support the effectiveness of SCDA's market basket survey, and (2) of the overall surveys' abilities to detect a broad number of

compounds in similar mean concentrations. However, the sample size might also be too small to detect any differences that may exist.

Matrix & Compound Property Effects

The only conclusions that can be drawn from the linear regression models and t-tests presented thus far are broad. At best, the t-test results imply that the two pesticide survey methods don't differ significantly with respect to both matrix and compound, except in several scenarios with the largest number of observations (Tables 5.3 & 5.4). Regression models offer some means of predictability of one survey's outcome, but typically the models' parameter estimates have relatively large standard errors. Therefore, certain intrinsic characteristics of the individual residues as well as properties of the commodities they were found in were examined as an attempt to observe the underlying reasons for significant differences detection between the two surveys.

To begin, the most recent paired dataset was isolated (2014). Sample standard deviations were calculated for each specific matrix-compound pair in each survey (provided that there were at least two detections in the SCDA method; the PDP method most often had sufficient detections). Corresponding relative standard deviations (RSD) were then obtained to ensure positive, dimensionless values (RSD is also known as the "Coefficient of Variation"). Finally, the difference between the two surveys' RSDs was calculated and absolute value was taken to maintain positive numbers. For example, in 2014 SCDA detected the compound boscalid seven times in apples at a mean concentration of 0.04 ppm with standard deviation of almost 0.03 ppm (rounded) and a large RSD of 69%. The analogous RSD for the same matrix-compound pair in the PDP survey was 135% for an absolute difference of 66% RSD. This indicates the detections

were nearly twice as variable in the PDP method as compared to the SCDA method. The RSDs of the PDP detections were larger than those in the SCDA method roughly two-thirds of the time.

Properties of the compounds of interest were obtained by searching an EPA database of physical/chemical property and environmental fate estimation known as Estimation Programs Interface Suite (EPI Suite). The properties of interest for each compound are:

- (1) Water solubility – the mass of a compound that will dissolve in 1 liter of water at room temperature (in mg/L).
- (2) Volatility – the tendency of a substance to evaporate at room temperature (in atm*m³/mol).
- (3) Vapor Pressure – the pressure exerted by a substance’s vapor when in equilibrium with its condensed phase at room temperature (in mm Hg).
- (4) Log K_{o-w} – an estimate of a chemical’s tendency to partition itself between an organic phase and an aqueous phase (dimensionless).

Matrix properties were obtained via the Food Composition Database maintained and published online by the USDA’s Agricultural Research Service. The properties of interest for each matrix are (each listed as a percentage – grams per 100 grams of matrix):

- (1) Water content.
- (2) Total lipids (fat).

The properties described above were tabulated in Microsoft Excel along with the corresponding calculated absolute differences in RSD ($|\Delta\text{RSD}|$). The SAS Online Studio was used again to make linear regression models with $|\Delta\text{RSD}|$ as the dependent variable against the various properties. Because of detections of each compound in multiple matrices, the regression models must again be sorted by matrix. A

comprehensive regression model yields no useful information since there's too often multiple y values per each x value. For example, there are five differences in RSD for the compound boscalid (one for each matrix in which it was detected). A plot of each of the five absolute RSD differences against the same log K_{O-w} would yield a vertical line with undefined slope. The regression models can be found in Table 5.11 on the following page.

Much like the regression models of paired detection means discussed earlier in this chapter, the results of Table 5.11 don't seem to indicate any significant trends. However, when viewing the result data, it is important to remember the scope of what the models represent. Alone, $|\Delta RSD|$ is the difference in how precise each survey method's data is. Therefore, a small $|\Delta RSD|$ would indicate that the variance in each survey's detections for a specific matrix-compound combination were relatively similar. That is, both methods had detections either tightly clustered around the mean or were both fairly spread out. Alternatively, a large $|\Delta RSD|$ would indicate that one survey's detections were significantly more precise than the other. $|\Delta RSD|$ ranged from as low as 1.5% to as much as 155% and there's little evidence of either compound- or matrix-specific trends in $|\Delta RSD|$. A positive slope in these regression models would indicate that the difference in the surveys' RSD grows with increasing numerical value of the property being modeled. The models for both compound vapor pressure and volatility are similar in that the estimated slopes and their associated errors are all extremely large which makes sense as the two properties are related to one another (the higher a substance's vapor pressure, the higher its volatility). What's curious is why the signs of the slopes for the bean matrix do not mimic one another but do match for all other matrices. The models for log K_{O-w} and

Table 5.11: Regression Models per Intrinsic Properties (Compound-Removed)

| Δ RSD| vs. Compound Vapor Pressure

Matrix	n	Y-int	(error)	Slope	(error)	r ²	Root MSE
Apple	3	90.50	(24.52)	6.7E+04	(4.4E+04)	0.70	34.6807
Bean	5	33.13	(9.08)	-4.02E+02	(3.0E+02)	0.38	18.1550
Blueberry	8	61.39	(19.32)	-7.4E+04	(4.2E+05)	0.01	48.8731
Peach	3	32.18	(9.45)	-7.7E+05	(4.1E+05)	0.78	13.3115
Strawberry	5	17.52	(12.08)	1.7E+06	(6.8E+05)	0.69	23.7386

| Δ RSD| vs. Compound Volatility

Matrix	n	Y-int	(error)	Slope	(error)	r ²	Root MSE
Apple	3	90.50	(24.52)	2.4E+07	(1.6E+07)	0.70	34.6805
Bean	5	21.93	(11.36)	2.0E+07	(2.3E+07)	0.20	20.5871
Blueberry	8	61.52	(20.73)	-3.7E+06	(2.6E+07)	0.00	48.9132
Peach	3	41.61	(5.50)	-4.9E+08	(1.1E+08)	0.96	5.9917
Strawberry	5	25.51	(20.18)	3.2E+07	(4.5E+07)	0.14	39.4535

| Δ RSD| vs. Compound log K_{O-w}

Matrix	n	Y-int	(error)	Slope	(error)	r ²	Root MSE
Apple	3	167.12	(129.94)	-17.74	(40.54)	0.16	58.1260
Bean	5	21.40	(12.72)	1.87	(2.55)	0.15	21.1606
Blueberry	8	81.12	(43.47)	-4.51	(8.49)	0.04	47.8876
Peach	3	43.31	(53.07)	-5.16	(12.24)	0.15	26.0898
Strawberry	5	1.58	(50.87)	6.59	(10.20)	0.12	39.8768

| Δ RSD| vs. Compound Water Solubility

Matrix	n	Y-int	(error)	Slope	(error)	r ²	Root MSE
Apple	3	105.54	(51.00)	0.05	(0.26)	0.03	62.3954
Bean	5	34.14	(11.70)	-4.75E-05	(5.3E-05)	0.21	20.4593
Blueberry	8	67.13	(22.64)	-0.33	(0.67)	0.04	48.0651
Peach	3	10.64	(16.35)	0.54	(0.56)	0.49	20.2121
Strawberry	5	64.70	(29.85)	-2.36	(1.87)	0.35	34.3856

solubility display a similar trend with respect to slope as they should since these two intrinsic properties are also closely related (substances with higher K_{O-w} are more

hydrophobic). The corresponding slope values of these two regression models generally differ by at least one order of magnitude and take on opposite signs except in the case of the blueberry matrix.

Of all the models displayed in Table 5.11, there is just one incidence of good correlation. The model for compound volatility in peaches has correlation coefficient of 0.96 and a fairly small RMSE of about 6 (rounded) which indicates that the individual observations fit pretty well to the predicted regression line. If the model is accurate, the difference in the two surveys' RSD decreases quickly with increasing compound volatility. Recall however, that this only implies that both SCDA and PDP compound detections in peaches tend to behave in the same manner relative to each compound's respective mean detection.

In the following Table 5.12, the same $|\Delta\text{RSD}|$ values are modeled by compound rather than matrix. Nearly all parameter estimates' standard errors are larger in numerical magnitude than the estimates themselves (some of which are many times larger). Again, there is only one instance of a nicely correlated predictive model with relatively small standard errors, a relatively small RMSE, and a squared correlation coefficient of 0.99. The data support that the absolute difference between the two surveys' RSD of cyprodinil detections in all matrices is related to the matrices' inherent total lipid percent. According to the model, 99% of the total variance in $|\Delta\text{RSD}|$ of cyprodinil detections can be explained by the regression on matrix total lipid percentage. Whether the regression correlation of $|\Delta\text{RSD}|$ of this particular residue with matrix lipid percentage is anything more than coincidental remains to be seen.

Table 5.12: Regression Models per Intrinsic Properties (Matrix-Removed)

Δ RSD vs. % Water							
Compound	n	Y-int	(error)	Slope	(error)	r ²	Root MSE
Bifenthrin	5	-0.46	(391.70)	0.54	(4.30)	0.01	36.5673
Boscalid	5	243.88	(452.08)	-2.08	(5.07)	0.05	42.6277
Chlorothalonil	3	330.95	(393.49)	-3.17	(4.30)	0.35	38.0570
Cyprodinil	3	1302.85	(1539.79)	-13.88	(17.49)	0.39	85.3505

Δ RSD vs. % Lipid							
Compound	n	Y-int	(error)	Slope	(error)	r ²	Root MSE
Bifenthrin	5	66.47	(70.08)	-71.43	(277.16)	0.02	36.2649
Boscalid	5	79.44	(80.00)	-85.38	(318.10)	0.02	43.2901
Chlorothalonil	3	-9.64	(71.13)	223.72	(298.62)	0.36	37.8509
Cyprodinil	3	-476.22	(41.08)	1901.34	(139.17)	0.99	7.9543

CHAPTER 6

CONCLUSIONS AND DISCUSSION

The results presented in the previous chapter do not allow for many concrete, definitive conclusions to be drawn regarding whether one method of pesticide surveying is any better or worse than the other. There were plenty of instances where both surveys detected a chemical compound in a commodity at a similar frequency of detection and/or an average detected concentration. And to that end, such instances are pretty remarkable when considering the differences in sampling volumes between the two programs and the challenges associated with comparing results of datasets whose number of observations differ by one or two orders of magnitude. There were also sufficient cases of dissimilar pairing – those instances in which the surveys' paired frequencies and means were not even close in numerical values. Yet, in either case, when multiple paired observations were combined to make a regression model, some semblances of underlying trends and patterns start to emerge. Those patterns seem to self-enhance as the number of paired observations grows. Therefore, comparative studies like this one can only be strengthened by having a larger pool of data from which to work. From stronger comparative studies come more robust models and a greater ability for those in the proper positions to make the best possible decisions regarding public and environmental health and, hopefully, the future of our nation's food safety legislation.

In order to generate more robust models, greater attention needs to be given to programs such as South Carolina Department of Agriculture's market-basket survey.

Considering that agribusiness is a nearly \$42 billion industry in South Carolina, the relevance of studies like this one and the significance of the relationships that can be uncovered in their pursuit should be self-evident (London 2015).

If the PDP's survey results are considered the national standard with respect to pesticide residue monitoring as described in chapter one, then this study highlights, if only superficially, those areas where the market-basket survey either meets or does not meet the national standard. Though it may often be difficult to convince legislative bodies to increase annual fiscal budgets, the results of this study would indicate that programs like the SCDA's market-basket survey perform at their absolute best when sampling volumes are high. This study is justification enough for the need for increased attention to be given to several areas of the SCDA's Consumer Protection Division. The only feasible way to increase sampling volumes is by the addition of both sample collectors and lab analysts.

The State's fleet of inspectors is understaffed and overworked. The responsibilities given to one just inspector who is assigned to two counties are a daunting set. In addition to inspecting all scales and gasoline pumps, an inspector may be asked to stop mid-shift to drive two or more hours to investigate a consumer complaint. It is certainly easy to understand why some of the agency's annual inspection targets often go unmet. The department should seriously consider trying to add at least five to ten inspector positions over the next several years, assigning them to the counties surrounding the state's most densely populated areas. These areas are more likely to receive a high volume of complaints which slows the work progress of the local inspectors.

There is an equally great need to increase staffing in the chemical residue lab. If the agency were to increase sampling by strengthening the inspector staffing, the two laboratory analysts would then be overworked. As it stands now, the lab's workload is severely impacted by absences, whether expected or unexpected, and virtually inoperable when both analysts have to use leave. Laboratory instrumentation is sufficient as long as the lab's results on a standard reference material continuously fall within known parameters.

One area in need of major attention is in the protocols of the initial commodity sampling procedures. Unwritten guidelines or requests to not sample strawberries very often are counterproductive. The only guidance that should be given in the way of commodity choice is a mandate that PDP commodities should always make up a portion of an inspector's sample collection (recall again that PDP commodities are pre-determined). For example, assume that in a given year, PDP samples apples, lettuce, grapes, green beans, and carrots. SCDA inspectors should then sample at least a majority, if not all, of those commodities weekly. This approach would boost the number of paired observations between the two surveys while still allowing for SCDA (and similar state agencies) to collect a handful of data on other commodities.

Comparisons of the laboratory analytical methods which used to obtain the original detection data were not even addressed. Though differences certainly exist in residue analyses with respect to laboratory instrumentation, analytical reagents, and extraction procedures, there also exists a simpler commonality shared by all labs whose data was used in this study. Samples arrive at a lab in their original, as sold conditions with little chance of adulteration during transport between the collection sites and

laboratories. Test portions are measured and combined with a solvent into some sort of homogenization device (i.e. a high speed blender). The resulting blend is then filtered for particulates and concentrated which leaves a small vial containing only a few milliliters of sample extract for instrument analysis and the ultimate detection of any lingering chemical residues. So, a future study may elect to examine the intimate differences between laboratory analytical methods for further insight.

On this topic, a crucial necessity that should be addressed before going forward is the need for standard reference material development and/or improvement where it already exists. Without such a material, there is no definitive way to ascertain the validity of an individual lab's results. This is probably best evidenced by the regression models made on the differences in the two surveys' relative standard deviations versus characteristic properties of both matrix and compound. Of the 29 observations in that dataset, there were just seven occurrences (less than 25%) of a $|\Delta\text{RSD}|$ being less than 10%. Recall that a small difference in absolute RSD means that the data generated by both surveys had RSDs that were either equally small or equally large. In either case, RSDs that differ by only 10% or less would indicate uniform laboratory precision. Instead, 41% of the observations in that same dataset had a $|\Delta\text{RSD}|$ of 50% or greater, with several of those being well above 100% absolute difference in relative standard deviation. The t-tests discussed in the previous chapter seldom indicate evidence of significant differences in mean detections, but more often than not, the $|\Delta\text{RSD}|$ calculations demonstrate large differences in the distributions of individual detections about their respective means. When combined, this is evidence of either or both of two things being true: (1) the overall distribution of pesticide residues in the population of all

commodities covers a wide concentration range, and/or (2) the analytical methods used by each of these survey methods in detecting the residues, whether internally precise or not, are often not as precise in comparison to each other. Therefore, the development and use of a standard reference material would help to ensure that differences in laboratory precision could be attributed more to substantial analyte variance rather than to differences in laboratory analytical methods.

A primary goal of this study was to examine whether the findings of these two survey programs mimic one another in terms of (1) the frequency in which they find a given compound in a particular agricultural commodity, and (2) the average detected residue concentration. While there isn't conclusive evidence to support that a definite correlation exists, there also isn't conclusive evidence to indicate significant differences in the historical outcomes. The t-test results and linear regression models generally indicate that both surveys make similar findings over an entire year's worth of monitoring.

The filtering imposed on the original databases placed significant restrictions on the data in certain years. For example, recall that at least three paired observations were needed to construct linear regression models, and at least two paired observations were needed to employ the t-test. There were only seven matching commodities in 2010, four of which had only one matching compound detection. Two of the remaining three commodities had more than two residue detections in common. That left just two matrices with which to construct the compound-removed linear regression models, and three matrices with which to use a t-test for that year of interest. So, when considering how much data had to be left out due to insufficient numbers of observations, it is

somewhat remarkable that the models turned out as well as they did and indicative that an increase in available data for future comparative analyses may produce some very useful information.

A feasible way of obtaining more useful data would be through an ongoing interagency collaboration program, both between the States themselves and between the States and the USDA. To achieve this, the overall structure of each agency's sample collection methods, analytical laboratory techniques and SOPs need not be disturbed (save from the addition of a standard reference material as previously discussed). For example, currently the SCDA doesn't use its detection data beyond the data's immediate intended purpose which is to randomly screen agricultural commodities for pesticide residues and protect the safety of the South Carolina consumer by stopping sale of any commodity in which excessively high levels of pesticides are found. In general, once results leave the laboratory, no one within the agency archives it for tracking and trend-identifying purposes (The same is true, in general, of each of the other labs' annual data). As is usual at the state government level, resource restraints (mainly financial) as well as the primary need to uphold the agency's mission statement prevent justification of a dedicated archivist position. To summarize, gathering, storing, and tracking data simply for historical analyses doesn't figure into the goals of the SCDA's Consumer Protection Division.

The PDP however, does exist purely for historical and informative purposes. Therefore, the PDP could be greatly enhanced by including the residue detection data of all State Departments of Agriculture (or analogous agencies where applicable), and/or any private labs who would choose to participate. All that would be needed is the

infrastructure of a simple internet-accessible database for continuous upload of the detection data by participating labs.

Consider the design of the PDP with respect to (1) commodity sampling selection, (2) sampling volume, and (3) sampling geographical layout (review Table 3.1 on page 14 as an example). The architects behind the PDP aim to create a representative sample of the U.S. food supply year after year. The reality, however, is that even though the PDP's sampling volume dwarfs those of State monitoring programs such as SCDA's, it's still a very small sample of an enormous population – the population of all produce available for sale and consumption throughout the United States. Through a multistate, collaborative, data-sharing program, both sampled commodities and volume of data generated annually would increase exponentially with little to no adverse effects on the resources of either the PDP or other monitoring programs such as SCDA's market basket survey. And because the PDP's goal is primarily to collect information on the nation's food supply, it seems obvious that more data would only increase information thereby allowing for the best domestic policy decisions, and facilitating future public and environmental health studies.

The design of such a program could be very simple. First and foremost, both the PDP and State monitoring programs carry on their respective surveys just as they have been. However, the PDP would relay to all participating labs which commodities have been selected for surveying ahead of the commencement of sampling exercises. Labs would be encouraged, but not required, to sample some (or all) of the same commodities as frequently as possible (rotational schedules could be established) while also continuing to sample commodities not listed on the PDP's scope. As labs analyze the

samples, their detection data (including non-detects) can concurrently be entered to an online database.

Such a program would auto-generate data continuously and in less than a few years, the PDP would likely have collected more information about the nation's food supply than it has since the program began in 1991. If many labs were to participate, over time the PDP could track geographical trends which could be used by many researchers studying public and environmental health. Similarly, regression models such as those made in this study could be made and continuously improved upon as researchers develop a better understanding of how pesticide residues behave both overall and with respect to individual matrices, climate patterns, spatial or temporal boundaries, or any other unknown factors. As regression models improve, priority can be assigned to investigate health and environmental impacts of those compounds with best regression correlation. For example, if a good regression model can be constructed of a compound commonly detected in baby food, then longitudinal cohort studies based on that model can be designed and conducted in the following years.

To protect the integrity of the data and to maintain high numbers of distributor participation, it is imperative for the sample origin information to be kept blind on both sides of the database. That is, the participating labs should know nothing of the origin of PDP sampled commodities just as the PDP should not collect the same information (save for perhaps country of origin, if different than the U.S.) when data is uploaded. A cornerstone trait of the PDP is that sampling sites volunteer their participation, and avenues that might discourage such participation should be avoided.

One area of research this study did not address is in the non-detection of pesticide residues. Observations were justifiably discarded if a compound which was detected by the PDP was not even screened for by SCDA. However, occasionally, certain compounds were detected by the SCDA which were not screened for by the PDP. Reasons for this anomaly are unknown, but it is somewhat confusing given the more sensitive and sophisticated detection abilities of PDP's participating labs. For example, SCDA had detection data for the compound chlorothalonil 21 times among all paired commodities over the entire study (more often than any other compound) in concentrations as high as 0.5 ppm and as often as 50% in some matrices. Yet the PDP only had matching detection data in six of those 21 instances. The other 15 times, the compound was not even screened for by PDP. The chemical is used as broad-spectrum fungicide on crops such as tomatoes, onions, and potatoes among others (Toxipedia; "Chlorothalonil"), and is also linked to the decline in honeybee populations in that it may alter the bees' susceptibility to a certain gut pathogen (Pettis et al. 2013).

Combined results of programs such as the PDP and the market basket survey could also have important economic consequences for the U.S. and its involvement in international trade agreements. Some chemicals are banned from worldwide usage while others are only banned in certain countries. If a commodity is imported from parts of the world where new or U.S.-banned substances are permitted for use, yet that commodity isn't on the PDP's annual sampling radar, then State monitoring programs are the nation's only way of gathering residue data.

At a very basic level, this study demonstrates the need to continue each of these government-funded monitoring programs. The results also indicate that there is data

valuable to many parties (both public and private) to be discovered and relationships that can begin to be better understood with a small investment in the infrastructure of a shareable database. Beyond that, more comparative examinations on multiple pesticide surveys' results could hopefully lead to a statistically defensible comparison which could continue in perpetuity as the world faces future food production demands. Regression models using multiple factors to study matrix and compound property effects might also lead to the development of commodity-specific compounds rather than the broad-spectrum chemicals which are currently being used.

REFERENCES

- Baker, B.P., C. M. Benbrook, E. Groth III, and K. Lutz Benbrook. 2002. "Pesticide Residues in Conventional, Integrated Pest Management (IPM)-grown and Foods: Insights from Three US Data Sets." *Food Additives & Contaminants*, 19:427-46. Accessed July 17, 2016. doi:10.1080/02652030110113799.
- Bempah, C. K., Jacob Asomaning, and Juliana Boateng. 2013. "Market Basket Survey for Some Pesticides Residues in Fruits and Vegetables from Ghana." *Journal of Microbiology, Biotechnology, and Food Sciences*. 2:850-71.
- Bertolote, J. M., A. Fleischmann, M. Eddleston and D. Gunnell. 2006. "Deaths from Pesticide Poisoning: A Global Response." *British Journal of Psychiatry*. 189:201-03. Accessed January 11, 2017. doi:10.1192/bjp.bp.105.020834.
- Centers for Disease Control and Prevention. "Estimates of Foodborne Illness in the United States." Last updated July 15, 2016. Accessed January 17, 2017. <https://www.cdc.gov/foodborneburden/2011-foodborne-estimates.html>.
- Estimation Programs Interface Suite™ (v. 4.11 for Microsoft® Windows). United States Environmental Protection Agency, Washington, DC, USA. Accessed February 8, 2017. <https://www.epa.gov/tsca-screening-tools/epi-suitetm-estimation-program-interface#what>.
- Gillespie, Gilbert, Duncan L. Hilchey, C. Clare Hinrichs, and Gail Feenstra. 2007. "Farmers' Markets as Keystones in Rebuilding Local and Regional Food Systems." In *Remaking the North American Food System, Strategies for Sustainability*, edited by C. Clare Hinrichs, and Thomas A. Lyson, 65-83. Lincoln: University of Nebraska Press.
- London, James B. 2015 "The Impact of the Agribusiness Sector on the South Carolina Economy." Report Commissioned by Palmetto AgriBusiness Council, South Carolina Department of Agriculture, South Carolina Farm Bureau, and Clemson University Public Service Activities." Accessed April 10, 2017. <http://www.scagribusiness.org/impact.php>.
- Lu, Chensheng, Kathryn Toepel, Rene Irish, Richard A. Fenske, Dana B. Barr, and Roberto Bravo. 2006. "Organic Diets Significantly Lower Children's Dietary Exposure to Organophosphorus Pesticides." *Environmental Health Perspectives* 114:260–63. Accessed January 8, 2017. www.jstor.org/stable/3436519

- Mills, Paul K. 1998. "Correlation Analysis of Pesticide Use Data and Cancer Incidence Rates in California Counties." *Archives of Environmental Health: An International Journal*, 53:410-13. Accessed December 28, 2016. doi:10.1080/00039899809605729. Murray, Kyle E., Sheeba M. Thomas, and Adria A. Bodour. 2010. "Prioritizing Research for Trace Pollutants and Emerging Contaminants in the Freshwater Environment." *Environmental Pollution* 158:3462-71. Accessed February 5, 2017. doi:10.1016/j.envpol.2010.08.009.
- Newsome, W. Harvey, Josee Doucet, David Davies, and W. F. Sun. 2000. "Pesticide Residues in the Canadian Market Basket Survey 1992 to 1996." *Food Additives & Contaminants* 17:847-54. Accessed July 13, 2016. doi:10.1080/026520300420411.
- National Sustainable Agriculture Coalition. "(FSMA) Overview and Background." Accessed January 17, 2017. <http://sustainableagriculture.net/fsma/overview-and-background/>.
- National Nutrient Database for Standard Reference. Release 28. United States Department of Agriculture, Agricultural Research Service, Nutrient Data Laboratory. Last updated May 2016. Accessed February 12, 2017. <https://ndb.nal.usda.gov/ndb/>.
- Northern Territory Department of Health. *Northern Territory Market Basket Survey 2014*. Accessed January 12, 2017. <http://hdl.handle.net/10137/616>.
- Pesticide Data Program Database Search Utility. Version 6.3. United States Department of Agriculture, Agricultural Marketing Service. Accessed October 20, 2016. <https://www.ams.usda.gov/datasets/pdp/pdpdata>.
- Pettis, Jeffery S., Elinor M. Lichtenberg, Michael Andree, Jennie Stitzinger, Robyn Rose, and Dennis vanEngelsdorp. 2013. "Crop Pollination Exposes Honey Bees to Pesticides Which Alters Their Susceptibility to the Gut Pathogen *Nosema ceranae*." *PLoS ONE* 8(7): e70182. Accessed March 1, 2017. doi:10.1371/journal.pone.0070182.
- Radwan, Mohamed A., and Ahmed K. Salama. 2006. "Market Basket Survey for Some Heavy Metals in Egyptian Fruits and Vegetables." *Food and Chemical Toxicology* 44:1273-78. Accessed January 7, 2017. doi:10.1016/j.fct.2006.02.004.
- Sahota, Amarjit. 2009 "The Global Market for Organic Food and Drink." In *The World of Organic Agriculture. Statistics and Emerging Trends 2009*, edited by Helga Willer and Lukas Kilcher, 59-63. FiBL-IFOAM Report. IFOAM, Bonn; FiBL, Frick; ITC, Geneva.

- Scallan, Elaine, Patricia M. Griffin, Frederick J. Angulo, Robert V. Tauxe, and Robert M. Hoekstra. 2011. "Foodborne Illness Acquired in the United States – Unspecified Agents." *Emerging Infectious Diseases*. 17:16-22. Accessed January 6, 2017. doi:10.3201/eid1701.P21101.
- Schechter, Arnold, Justin Colacino, Darrah Haffner, Keyur Patel, Matthias Opel, Olaf Pöpke, and Linda Birnbaum. 2010. "Perfluorinated Compounds, Polychlorinated Biphenyls, and Organochlorine Pesticide Contamination in Composite Food Samples from Dallas, Texas, USA." *Environmental Health Perspectives* 118: 796-802. Accessed July 24, 2016. doi:10.1289/ehp.0901347.
- South Carolina Department of Agriculture. "Our Mission." Accessed January 20, 2017. <http://agriculture.sc.gov> (scrolling headline on homepage).
- South Carolina Department of Agriculture, Chemical Residue Lab. Annual Summary Report, Fiscal Years 2009-10, 2010-11, 2011-12, 2012-13, 2013-14, and 2014-15. Edited by Sherry Garris. Available by request. <http://agriculture.sc.gov/divisions/consumer-protection/lab-services/>.
- Toxipedia. "Chlorothalonil." Lead author Elliott Thoreby. Lead editor Maria M. Williams. Last updated May 13, 2011. Accessed March 10, 2017. <http://www.toxipedia.org/display/toxipedia/Chlorothalonil>.
- United States Department of Agriculture, Agricultural Marketing Service. *Pesticide Data Program Annual Summary, Calendar Year 2011*. Pages 1-8. Published 2013. Accessed July 7, 2016. <https://www.ams.usda.gov/datasets/pdp/pdpdata>.
- United States Food and Drug Administration. "FDA Food Safety Modernization Act (FSMA)." Last updated April 20, 2017. Accessed January 17, 2017. <http://www.fda.gov/Food/GuidanceRegulation/FSMA/>.
- Williams, P. N., A. Raab, J. Feldmann, and A. A. Meharg. 2007. "Market Basket Survey Shows Elevated Levels of As in South Central U.S. Processed Rice Compared to California: Consequences for Human Dietary Exposure." *Environmental Science & Technology* 41:2178-83. Accessed January 7, 2017. doi: 10.1021/es061489k.