Levels of Selected Pyrethroids in the Work Environment of Pest Control Service Technicians and the Potential for Take-Home Exposure

by

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DEDICATION

I would like to dedicate this work to each member of my family. They were very supportive throughout my trek along this journey. In pursuit of this academic milestone, I missed out on some very valuable and irreplaceable family time. I owe a huge debt to my son for missing out on some of his games at school. Nonetheless, their continuous outpouring of love, support and words of encouragement have kept me humbled and focused on the goal ahead. You have taught me that team work and resilience are two integral hallmarks of success.

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ABSTRACT

Pyrethroid insecticides are widely used in pest control where pest control service technicians (PCSTs) could be chronically exposed. Levels of six pyrethroids were quantified in air and dust inside storage depots of pest control companies and inside both service and private vehicles of PCSTs. Levels of pyrethroids were also quantified in the socks that PCSTs wore. Samples were analyzed using gas chromatography/mass spectrometry (GC/MS) and exposure levels in ingestible dust among the PCSTs calculated.

The highest levels of individual pyrethroids found in the air samples were 3631ng/m^3 of cyfluthrin in service vehicles, 287 ng/m^3 of cypermethrin in personal vehicles and 163ng/m^3 of cypermethrin in storage depots. The highest levels of individual pyrethroids found in dust were 426,531 ng/g of permethrin in services vehicle, 43,605 ng/g of cyfluthrin in personal vehicles and 1,050249 ng/g of cyfluthrin in storage depots. The levels in socks were as high as milligrams per pair of socks.

These levels suggest a high possibility that applicators are being exposed to substantial levels of pyrethroids in their work environments, especially via dust inhalation. Exposure calculations using the total pyrethroid levels in dust found in service and personal vehicles and storage depots ranged from 0.022 ng/kg/day to 74.993 ng/kg/day. High pyrethroid levels found in socks and personal vehicles suggest that applicators may be inadvertently transporting pyrethroids into their homes, especially

those with little experience and those who engage in poor hygiene practices at work. This data can be useful in educating pest control service technicians on the safe use of pyrethroids.

CHAPTER 1 – INTRODUCTION

Background

There are a number of sub-categories of insecticides that are widely used in the pest control industry. One of the main sub-categories is called pyrethroids. Pyrethroids are substances that can pose serious health hazards. In fact, the United States Department of Health and Human Services (USDHHS, 2003) reported that pyrethroids are suspected of being carcinogenic, and Chen & Zhang (1991) reported that pyrethroids have been found to cause nervous sensitization and dizziness, among other symptoms, in workers who apply pyrethroids. Although a few studies have found a possible association between exposure to pyrethroids and chronic illnesses in humans (Rusiecki et al., 2009), there are those who have refuted such conclusions (Kolaczinski & Curtis, 2004). Nonetheless, even skeptics such as Kolaczinski & Curtis (2004) suggest that chronic effects due to exposure to pyrethroids cannot be decisively ruled out.

Pest Control Service Technicians (PCSTs) are exposed to these substances on a daily basis, especially during peak application periods. The probability for inhalation and dermal exposure may also vary depending on the concentration levels present in different matrices in the work environment. Some of these matrices include: dust, air and personal protective equipment (PPE).

In fact, empirical evidence has proven that residues from some insecticides have been transferred from the workplace to pesticide applicators and from these applicators to

homes, where families can be affected (Coronado et al., 2006). Both the Occupational Safety and Health Act (OSHA, 1970) and the Workers' Family Protection Act (WFPA, 1992) have also acknowledged that hazardous substances exist in the workplace and are sometimes conveyed home. OSHA also argues that this can be decreased and/or prevented through education programs, by facilitating workplace hazard reduction, and by encouraging stakeholders to establish or enhance programs for providing safer work environments (OSHA, 1970).

Despite the aforementioned considerations, a knowledge gap still exists regarding contaminants in the workplace and how they are transferred to the home environment (WFPA, 1992). This research seeks to narrow this gap by informing on levels of pyrethroids that can be quantified in the work environment of pest control technicians, and the potential for take home exposure. Using the results of this research, we can ascertain if higher levels of training, more experience and adherence to stringent hygienic practices among pest control technicians correlates to diminish the potential for take-home exposure.

Definition of Terms

Acute Exposure - Exposure to a chemical for duration of 14 days or less as specified in its toxicological profiles (USDHHS, 2003).

Chronic Exposure - Exposure to a chemical for 365 days or more as specified in its toxicological profiles (USDHHS, 2003).

Half-life- A measure of rate for the time required to eliminate one half of the quantity of a chemical from the body or an environmental media (USDHHS. 2003).

Indoor dust - "particles found in the interior of a building that have settled onto objects, surfaces, floors and carpeting. It may also include soil particles that have been tracked or blown into the indoor environment from outdoors" (U.S.EPA, 2011).

Intermediate Exposure - Exposure to a chemical for a duration of 15-364 days as specified in its toxicological profiles (USDHHS, 2003).

LD_{50} . Lethal Dose $_{50}$ - The dose of a chemical which has been calculated to cause death in 50% of a defined experimental animal population (USDHHS, 2003).

Pesticide exposure - occurs by swallowing, breathing or by its interaction with the skin or eyes. Impact from the exposure can occur over the short term, it can occur intermediately and it can also be chronic (ATSDR, 2009).

Pyrethroid - Pyrethrum is a naturally accruing mixture of chemicals found in certain chrysanthemum flowers. Synthetic pyrethroids are similar in structure to pyrethrins but have greater insecticidal activity and toxicity to mammals and last longer in the environment. Most pyrethroids are comprised of several molecules having the same

chemical formula with atoms joined in the same sequence but the atoms are arranged differently in space (USDHHS, 2003).

Restricted use pesticides (RUPs) - The RUP designation holds that a pesticide falls into this category when its use in accordance with the prescribed directions on the labels still has the potential to cause significant sub chronic, chronic or delayed toxicological effects on humans whether from single or multiple exposures (Florida Statutes, Chapter 487.042).

Take home exposure - Refers to the transport of contaminants from the workplace to the residence on a worker's person or clothing (Curl et al., 2002).

The Evolution and Classification of Pyrethroids

The flowers of the Chrysanthemum *cineum* and Chrysanthemum *cinerariaefolium* have historically been known to have insecticidal properties. The flowers have been crushed and chemicals extracted for the production of pyrethrum, which contains the insecticidal pyrethrins. Pyrethroids, the synthetic equivalents of pyrethrins, have been manufactured for increased environmental stability (USDHHS, 2003). Pyrethroids are placed into two broad classes: Type 1 and Type II Pyrethroids. The categories are based on the insecticides lethal and physical properties. Schleier & Peterson (2011) postulated that "the effect of each type is evidenced by differences in body tremors in tested rats following ingestion of a lethal dose." Pyrethrins and pyrethroids are considered to be

effective insect control agents with low mammalian toxicity and low environmental persistence. However, some formulations of pyrethroids such as granular and emulsified concentrates have the potential to cause harm even when they are used according to the label directions. These formulations are classified as restricted-use pesticides (RUPs). Some formulations may also contain other potentially toxic ingredients such as synergists, which can result in further toxicity depending on the levels of exposure (USDHHS, 2003).

Most commercially available pyrethroids are comprised of multiple compounds called stereoisomers. Stereoisomers are molecules which have similar chemical formula, where the atoms are joined in a similar order, but they are unlike in the spatial arrangements of the atoms (USDHHS, 2003). Given the complex nature of pyrethroids, some of the technical grades of pyrethroid insecticides are comprised of multiple stereoisomers, and a single pyrethroid could contain of up to eight stereoisomers. Consequently, it is expected that multiple isomers may be detected during the analysis of samples which contain any amount of the targeted pyrethroids.

Toxicological Properties of Selected Pyrethroids

The Pyrethroids pesticide class is considered safer than organochlorines, organophosphates and carbamates pesticides (Lopez et al., 2005), which were widely used prior to widespread use of pyrethroids. Pyrethroids are also considered less toxic to mammals (USDHHS, 2003). They are neurotoxins which act on the sodium channel of the nervous system of affected animals. That is, they disrupt the transmission of nerve

impulses (USDHHS, 2003), an effect which also varies between Type I and Type II pyrethroids.

Key criteria used to classify individual pyrethroids include the presence/absence of a nitrile functional group, the position of such a functional group, and the symptoms produced by them (USDHHS, 2003). Type I pyrethroids do not contain the nitrile functional group. Test rats that have ingested a lethal dose of Type I pyrethroids immediately become aggressive, show increased sensitivity followed by fine shivering, prostration, shivering throughout the entire body, and an increase in body temperature followed by death. The Type II pyrethroids have the nitrile functional group and produce severe toxicological effects. Rats that ingested type II pyrethroids produce acute neurological symptoms such as excessive salivation, escalated response when startled and a complete body shiver (USDHHS, 2003; Kolaczinski & Curtis 2004).

Just as exposure to pyrethroids results in toxic effects on rats, so it is that signs of pyrethroid poisoning can also exist in humans, particularly when they are exposed to these chemicals through job-related activities such as interaction with unprotected skin (Chen et al., 1991). Carcinogenicity studies have also led to the classification of some pyrethroids as a "likely human carcinogen when a person is exposed to them orally" (USDHHS, 2003; USEPA, 2014). Ingestion is a real possibility if contaminated dust particles are taken home in service or personal vehicles driven by pest control service technicians or when family members are exposed to pyrethroids residues transferred home on the technician's person or on personal protective equipment worn by the

technician. Service technicians who do not observe proper personal hygiene or use protective gear or equipment can also experience oral and dermal exposure.

Pyrethroids formulations that have a restricted use pesticide (RUP) designation are classified as such based upon their potential to cause harm, or because they contain other potentially toxic ingredients which can also be hazardous following exposure (USDHHS, 2003). The RUP designation holds that a pesticide falls into this category when, despite its use in accordance with prescribed label directions it still has the potential to cause significant sub chronic, chronic or delayed toxicological effects on humans whether from a singular or multiple exposures (Florida Statutes, Chapter 487.042) Damalas & Eleftherohorinos (2011) stated that the low toxicity of pyrethroids does not mean that they do not pose health risks to humans. El-Magd and Shoukry (2011) reported that "the possible effects of continued exposure were demonstrated when workers in a pyrethroids-manufacturing company were found to have developed endocrine disruption and respiratory, as well as liver, malfunction amongst other problems." In the study by El-Magd and Shoukry, eighteen workers in the pyrethroid manufacturing facility were compared with a control group of twenty unexposed individuals. The workers who were exposed to pyrethroids had far more incidences of headache, coughing and wheezing. Therefore, the authors concluded that exposure to pyrethroids could produce chronic effects such as endocrine disturbances and acute respiratory ailments among others. (El-Magd and Shoukry, 2011).

According to Chen et al. (1991), other studies have also pointed to malignant effects associated with the regular usage of this category of pesticides. One

epidemiological study found that out of 3,113 men who were involved in pyrethroids application, 834 of them had nervous sensitization in their faces, and some even had systemic symptoms associated with acute pyrethroids poisoning. These systemic symptoms included: dizziness, headache and fatigue. Providing evidence regarding how widespread the exposure to pyrethroids has been, Karret al. (2007) explained that pyrethroids were ranked close to organophosphates, followed by DEET and rodenticides, as the leading cause of pesticide-related illnesses in the United States.

The acute toxicity of a pesticide is measured by its LD_{50}, which refers to the concentration of the pesticide at which a single dosage will result in death of fifty percent of the test population. Rats are commonly used in studies to ascertain LD_{50} of pesticides and as a proxy of possible toxicity to humans (Johnson et al., 2010). Table I displays the mammalian toxicities of the pyrethroids of interest to this study.

Table 1: Mammalian Toxicities (mg/kg) of body weight of the pyrethroids targeted in this study.

Common Name	Rat Oral LD_{50}	Rabbit Dermal LD_{50}
Allethrin [a]	860	11332
Bifenthrin [b]	53.4-210.4	2000
Cyfluthrin [a]	869-1271	>5000 Rat
Cypermethrin [a]	250	>2000
Deltamethrin [a]	31-139	>2000
Permethrin [c]	430-4000	>2000

Note:.Compiled from [a] (Fischel, 2014), [b] (Johnson et al., 2010), [and c] (Toynton et al., 2009)

Use of Pyrethroids in the Pest Control Industry in Florida

There are approximately 3900 pest control companies in the state of Florida that are licensed to offer pest control services. These companies employ as many as 45,000 PCST who possess state-issued identification cards to practice pest control (J.E Parker Florida Department of Agriculture and Consumer Service, personal communication, February 2013). These individuals and firms have the ability to practice Lawn and Ornamental Pest Control (L&O), General Household Pest Control (GHP) and Termite Control (TC). Some of the insecticides that are widely used in all three categories of pest control fall under the umbrella term 'pyrethroids'. Moreover, pyrethroids and pyrethroid-containing compounds account for nine out of the fourteen insecticides which have been registered for the control of the Southern Chinch bug. The Southern Chinch bug is the most dominant lawn pest in the State of Florida (Buss, 2010).

The preponderant usage of pyrethroids in Florida can also be gleaned from statistics which have been archived in the National Pesticide Information Retrieval System (NPIRS) database. The data show that 413 Florida companies distribute/sell or manufacture pyrethroids. The six most commonly used pyrethroids, which were selected for this study all appear in the NPIRS database (NPIRS, 2013).

In an attempt to educate individuals regarding the use of pyrethroids, the United States Environmental Protection Agency (U.S.EPA, 2012) reported that pyrethroids form some of the most popular ingredients in restricted use pesticides. Furthermore, about a quarter of the pesticides used in the United States are classified as RUPs. Many of the current brands of pesticides which are registered and listed for usage in Florida contain a

significant quantity of pyrethroid active ingredients. The number of products which were retrieved from the NPIRS database that list popular pyrethroids ingredients are as follows: Bifenthrin - 57, Abamectin - 1, Cypermethrin - 21, Cyfluthrin - 8, Resmethrin - 2,Permethrin – 21, Deltamethrin – 1, and Allethrin - 0 (NPIRS, 2013). Although the search for Allethrin may indicate a zero return, this is not an indication that it is not being used in Florida. In fact, Allethrin was found in pesticide storage facilities or was being used by the companies which participated in this study.

Take-Home Exposure

Pesticide exposure occurs by swallowing, breathing or by its interaction with the skin or eyes. Impact from the exposure can occur over the short term, it can occur intermediately and it can also be chronic (ATSDR, 2009).

Because different types of illnesses may occur over varied time periods and the symptoms may manifest themselves in different ways, it follows that exposure to pesticides is defined at all three levels: an acute exposure to pesticides occurs for fourteen (14) days, an intermediate exposure can last anywhere between 14 to 90 days, and a chronic exposure usually occurs for more than a year (ATSDR, 2009).

In a 1992 report submitted to Congress to address the transfer of pesticide residues from the workplace to people's homes (Workers Family Protection Act WFPA, 1992) it was stated that greater concentrations of pesticides were found in the homes of farm workers as opposed to persons who were not involved in farm work. This discovery

supports the notion that work gear, equipment, personal and service vehicles, and clothing items can be sources of in-home contaminants.

Such discovery is also consistent with the conclusions of Karr et al. (2007) and Damalas and Eleftherohorinos (2011) that "those who work with pesticides should understand the need for using personal protective equipment and their work clothes should be laundered separately since it is a possibility that they might expose others in their homes to pesticide residues."

Damalas and Eleftherohorinos (2011) further stated that exposure to pesticides is also influenced by how often they are used and the duration of use. This may result in major differences in the effects of pesticide exposure on career pesticide applicators when compared to the effects on those who apply pesticide only seasonally.

Since exposure to pesticides in homes has been receiving some attention in the scientific literature, Fenske et al. (2000) examined dust samples and urine samples taken from the homes of both farm workers and non-farm workers. After the samples were analyzed, it was discovered that there were greater concentrations of organophosphate metabolites in urine and organophosphates in dust samples taken from the families that were affiliated with farming than the samples taken from homes of those with no affiliation with farming. The samples with higher concentrations revealed a direct correlation to pesticide application periods.

The quantity of pesticides handled at the workplace is also a major factor in determining the extent to which take -home pesticide exposure occurs. Lozier et al. (2012) is one study which detected higher loads of the pesticide atrazine in dust samples

taken from atrazine applicators homes in peak application periods when compared to dust samples taken in non-peak periods.

Coronado et al. (2006) also examined the take-home exposure pathway and its role in home organophosphates contamination. One hundred and fifty six (156) dust samples were taken from the homes of farm workers and 190 dust samples were taken from the vehicles used in their commute to work. In addition, 213 adult urine samples and 211 urine samples from the children of farm workers were tested. There was a strong and positive correlation between the quantities of azinphos-methyl, an organophosphate insecticide, found in the vehicles and household dust and its metabolites in the urine samples.

Clearly, pesticide residues which are present in dust could result in both inhalation and dermal exposure (USDHHS, 2003). Exposure levels may vary depending on the technicians' hygiene practices, and also on the type of application equipment used. (Harris et al., 2002). To limit take-home exposure, farm workers and PCSTs can leave soiled clothes at work (USDHHS, 1995). Laundering work clothes separately may also be helpful and is often suggested on pesticide labels.

A search of published literature on the subject yielded only one study in which pyrethroids were quantified in the work environment of pest control companies (Wright et al., 1996) and no studies were found that addressed take-home pyrethroids exposure. The bulk of published studies focus on organophosphates originating in agricultural and take-home exposure. At the same time, pyrethroids are widely used by pest control technicians. Similar to other pesticides, pyrethroid residues have the ability to persist in

the air and dust in work environments and can be transported to technicians' homes via their vehicles and clothes. Figure 1 identifies areas within pest control companies where pyrethroid residues are likely to accumulate. Thus, it is likely that measureable quantities of these compounds exist in these areas. Therefore, it would be beneficial to ascertain the level of occupational exposure and potential take home exposure to pyrethroids among PCSTs. This could be an important step in identifying actions to reduce pyrethroids loadings and to preserve the health and safety of service technicians and their families.

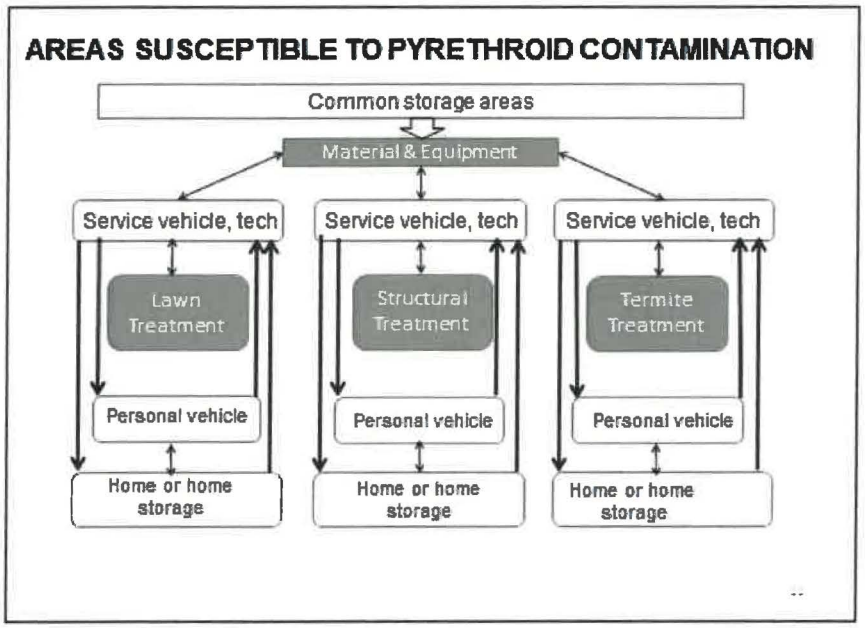


Figure 1: Some areas where pyrethroids residues may be conveyed and possible detection points at pest control companies.

Goals and Objectives

Since occupational and take home exposure routes consist of both air and dust in storage areas and personal and service vehicles, and the clothes or Personal Protective Equipment (PPE) worn by technicians, the goal of this research is to quantify the levels of selected pyrethroids present in the work environments and on clothing of PCSTs and to estimate the potential for take-home exposure. Specific objectives are to determine:

1. levels of pyrethroids to which applicators may be chronically exposed in storage areas/depots;
2. levels of pyrethroids in the work and personal vehicles of PCSTs;
3. levels of pyrethroids present in the work socks of PCSTs;
4. exposure levels in PCSTs via dust in storage areas and vehicles;
5. the potential for take-home exposure with respect to the selected pyrethroids; and,
6. whether technicians' training and experience and the extent to which hygiene play a role in the potential for take- home exposure.

CHAPTER 2 – LITERATURE REVIEW

Trends in the Development and Use of Pyrethroids

Although insecticides that contain pyrethroids have been in use since the 1950s (Palmquest et al., 2012), their wide scale use did not begin until the 1970s. One notable example of an earlier pyrethroid is permethrin which was found to be more stable in light and offered greater insecticidal activity when compared to previously used pyrethrins (Schleier and Peterson, 2011). The increase in usage of pyrethroids in the 1970s was concurrent with a decrease in the usage of organophosphates, carbamates, and organochlorines (USEPA, 2013; Schleier and Peterson, 2011). This transition has been quite noticeable throughout the pest control industry (Schleier and Peterson, 2011). Currently, at least 3500 registered products that contain pyrethroids and pyrethrins are used in household pest control and in agricultural pest control (USEPA, 2013). Pyrethrins and pyrethroids now account for approximately 23% of the world's insecticide market, and they are approved for use in both agricultural and non-agricultural industries (Schleier and Peterson, 2011).

The three most recent estimates of conventional pesticides' active ingredients used in the non-agricultural market sector (both home and garden component) give us an idea of how widely used pyrethroids are in the U.S. (USEPA, 2012). In 2001 alone, pyrethroid use was estimated to be one million pounds. By 2003, pyrethroids were ranked as the seventh most widely used active ingredients for pesticides in the U.S.; and were ranked the second highest in terms of quantity with an estimated 2-4 million pounds. The 2005 to 2007 survey of pesticide use reflected additional increases in pyrethroid usage; with a sixth (6^{th}) place ranking for the most commonly used pesticide active ingredient and while remaining the second most widely used insecticide nationally (USEPA, 2012).

It has been postulated that, on a national scale, it is likely that pyrethroids are more widely used in non-agricultural markets (Palmquest et al, 2012). In 2008, this was the case in California, the nation's largest producer of agricultural products. These non-agricultural applications include landscape, structural and public health pest control (Palmquest et al., 2012).

Chemical and Physical Properties of Pyrethroids in this study

Allethrin, bifenthrin, cyfluthrin, cypermethrin, deltamethrin and permethrin are some popular pyrethroid active ingredients in common insecticides. Their chemical identities and properties are detailed in Table 2.

Table 2: Chemical and physical properties of pyrethroids in this study.

Name	CAS #	Chemical and Physical Properties
Allethrin	584-79-2	Molecular Weight 304.2
		[a]Water solubility mg/L 4.6 (25 °C)
		Partition Coefficients:
		[a]Log K_{ow} 4.8
		[a]Vapor Pressure mmHg@25 °C $1.2x10^{-6}$ (21 °C)
		[a]Henrys Law Constant atm m^3 /mol @25 °C $6.1x10^{-7}$
		[b]Soil Sorption Coefficient $9.5 x10^3$
Cyfluthrin	68359-7-5	[a]Molecular Weight 453.3
		[a]Water solubility mg/L 0.002 (20 °C)
		Partition Coefficients:
		[a]Log Kow 5.94
		[a]Vapor Pressure mmHg@25 °C $2.03x10^{-9}$
		[a]Henrys Law Constant atm m^3 /mol @25 °C $9.5 x10^{-7}$
		[c]Soil Sorption Coefficient $6.24X10^4$
Cypermethrin	52918-63-5	[a]Molecular weight 416.3
		[a]Water solubility mg/L 0.004 (20 °C)
		Partition Coefficients:
		[a]Log Kow 6.6
		[a]Vapor Pressure mm Hg @20 °C $3.07x10^{-9}$
		[a]Henrys Law Constant atm m^3 /mol @25 °C $4.2 x10^{-7}$
		[b]Soil Sorption Coefficient $8.6x10^4$
Deltamethrin	52918-65	[d]Molecular Weight 505.2 g/mol
		[b]Water solubility mg/L 0 .002-0.0002
		Partition Coefficients:
		[a]Log Kow 6.1
		[db]Vapor Pressure mmHg@25 °C $1.5x10^{-8}$

		[a]Henrys Law Constant atm m^3 /mol @25 °C1.2 $x10^{-4}$
		[db]Soil Sorption Coefficient 7.05 $x10^5$ to 3.14$x10^6$
Bifenthrin	584-79-2	[a]Molecular Weight 422.9 g/mol
		[a]Water solubility mg/L 0 .1
		Partition Coefficients:
		[a]Log Kow 6.0
		[a]Vapor Pressure mmHg@25 °C 1.8$x10^{-4}$
		[a]Henrys Law Constant atm m^3 /mol @25 °C1.0 $x10^{-3}$
		[db]Soil Sorption Coefficient 1.3$x10^5$ to 3.0$x10^5$

Table 2. Chemical and physical properties of pyrethroids (continued.)

Name	CAS #	Chemical and Physical Properties
Permethrin	52645-53-1	Molecular Weight 391.3
		[a]Water solubility mg/L 0.006 (20 °C)
		Partition Coefficients:
		Log K_{ow} 6.5
		[a]Vapor Pressure mmHg@25 °C 2.2$x10^{-8}$ (25 °C)
		[a]Henrys Law Constant atm m^3 /mol @25°C 1.9x10 - 6
		[e]Soil Sorption Coefficient 1.0 $x10^5$

Note: [a] (USDHHS, 2003), [b](Kegley et al., 2014), [c] (Casijens, 2008), (Johnson et al., 2010), (Toynton et al., 2009)

In general terms, the water solubility, vapor pressure and Henrys Law Constants of pyrethroids are low while their octanol-water partitioning coefficient, K_{ow}, is high (USDHHS, 2003; Schleier, 2011). They bind readily to soil and sediments (Schleier, 2011) and the photochemical degradation of pyrethroids is rapid due to the formation of isomers from the substituent on the propane ring or to oxidation. Photochemical degradation is also due to the oxidation of their acid or alcohol components that are present in Type II pyrethroids (Schleier, 2011). Since a single pyrethroid may have various isomeric configurations, chemical, physical and toxicological properties may

vary (USDHHS, 2003). The structure of each of the target pyrethroids is shown in Figure 2 below.

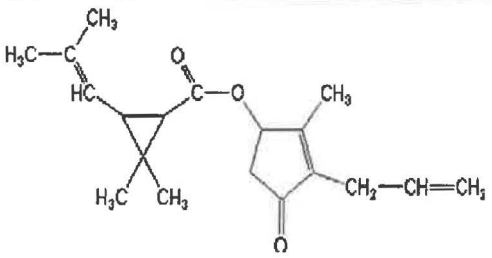
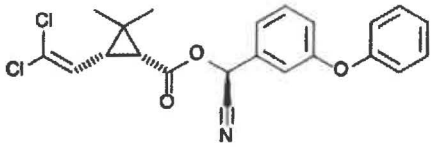
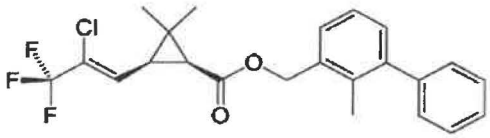
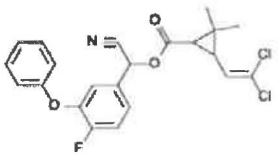
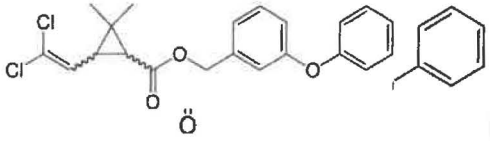
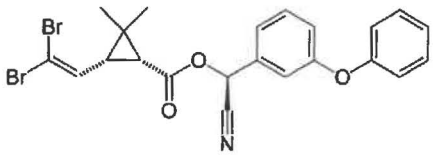
Type 1	**Type 11**
Allethrin	Cypermethrin
	
Bifenthrin	Cyfluthrin
	
Permethrin	Deltamethrin
	

Figure 2: Chemical structure of target pyrethroids.

The half-life of pesticides is another important chemical property which partially determines their environmental stability and impact. The half-life refers to the time it takes for a given amount of the pesticide to be reduced to one half of the original amount and is classified in terms of duration. If less than 16 days it is said to be low; moderate half-life ranges from 16-59 days and high half-life exceeds 60 days (Hansonet al., 2015). Environmental factors such as water, soil, light, and air influence pesticide half-lives and thus could have had an effect on the measured levels of pyrethroids in the matrices in which they are quantified in this study. Table 3 shows the half-life values of the target pesticides.

Table 3: Half-Life of targeted pyrethroids:

Pyrethroid	Hydrolysis			Photolysis		Soil degradation	
	pH 5	pH7	pH 9	Water	Soil	Aerobic	Anaerobic
Allethrin		HAC [h]		RD [h]		60 [h]	32 [g]
Bifenthrin	s**			276-416[j]	106-147 [j]	97-250 [j]	
Cyfluthrin		193a		12.2 b	2-16 c	63e	33.6 [d]
Cypermethrin [i]	619	271	1.9	30.1	165	27.6	55
Deltamethrin [i]	S	s	2.15	55.5	34.7	24.2	28.9
Permethrin	-	-	-	19-27 hrs [k]	-	11.6-113[k]	

[a] @25°C ; [b]@ 25°C & pH5 ;[c] @28°C pH 6.6 in sandy loam; [d] loam; [e] 25°C pH 9 Sandy loam; [f] all from Casjens Environmental fate of cyfluthrin; [g] from Kegley et al (2014); [h] University of Hertfordshire (2013); [i] all from Schleier, J.(2011); [j]Johnson et al(2010); [k] Toynton et al (2009); [l] Extension Toxicology Network (1996); * In distilled water; [m] S = Stable ; Fecko, A. (1999) S**= Stable at pH 6.7 and R25°C Feco; D = Rapid decomposition @ pH 7 in uv light; HAC = hydrolyses under alkaline conditions

Contaminated Indoor Dust: An Exposure Route to Pesticides

Indoor dust consists of "particles found in the interior of a building that have settled onto objects, surfaces, floors and carpeting. It may also include soil particles that have been tracked or blown into the indoor environment from outdoors" (U.S.EPA, 2011). Indoor dusts can also be defined as dusts which may be found in service or personal vehicles used by PCSTs. Dust found in personal vehicles used to commute to and from work or found in pesticide storage areas fits this general definition. Dust is a sufficiently stable matrix so that contaminated indoor dust is seen as an indicator of potential indoor pesticide exposure (Quiros et al., 2011). The ability of indoor dust to store and concentrate organic contaminants also qualifies it as a suitable proxy when assessing the likelihood of exposure to contaminants indoors. Furthermore, there is a tendency for greater exposure to chemical residues indoors due to the fact that dust-bound organic contaminants persist in these environments as photolysis, volatilization and because other processes that cause degradation in outdoor environments are usually lacking or ameliorated indoors (Hwang et al., 2008).

Pesticide in Dust from Work Vehicles

Measureable levels of pesticides such as pyrethroids can be tracked from their application sites into vehicles and into buildings following application (Coronado et al, 2006). Fenske et al. (2013) not only detected the organophosphate pesticides azinphosmethyl, phosmet, chlorpyrifos and malathion in vehicular dust samples, but they

further argued that a vehicle used for transportation to and from work could transport pesticides that end up in the home environment. Similarly, Curl et al. (2002) detected these same organophosphates, in addition to diazinon and methyl-parathion, in dust samples taken from the vehicles that pesticide handlers used to travel to and from their jobs. Other studies documenting detections of pesticides in vehicular dust include: Coronado et al. (2006); Curl et al. (2002); Higgins et al. (2001); and Thompson et al. (2003). These reports mostly identified organophosphates and they focused primarily on agricultural workers. Interestingly, these same studies also reported on levels of organophosphate detected in the homes of farm workers involved in pesticide application or other farming activities. These studies all suggested the occurrence of take-home exposure.

In the case of commercial pest control operators, Lozier et al. (2012) argued that persons can be exposed to pesticides by coming in contact with dust particles lodged in their vehicles. Lozier et al (2012) also reported the detection of the highest loads of atrazine, 2.68 ng/cm^2, in dust particles taken from entry ways where commercial pesticide applicators changed their boots and entered homes. Besides the 2.68 ng/cm^2 detected in entry ways, 0.18 ng /cm^2, 0.44 ng /cm^2 and 0.47 ng/cm^2 were also detected in living rooms, master bedrooms and the kitchens of those commercial pesticide applicators. And, although dust samples were not taken from the commuters' vehicles, the presence of atrazine residues on their boots suggests the likelihood that the driver or passenger foot wells of the commuter vehicles could play a role in conveying these residues.

Pyrethroids Detection in Indoor Dust

Although the pesticides which belong to the class of pyrethroids are less persistent and environmentally stable when compared to organochlorines (Palmquest et al., 2012), some studies documented persistence and subsequent detection of pyrethroid pesticides indoors. Detection of pesticide residues under these conditions is not surprising as their residues are likely to last for longer periods under indoor conditions. This is due to the absence of environmental factors such as microbes, sun and precipitation, all of which foster degradation (McCauley et al., 2001; Hwang et al., 2008). Consistent with these findings, Quiros et al. (2011) analyzed 54 indoor dust samples taken from carpeted areas within agricultural and urban households. Most of the participants reported pyrethroid use in their homes within the three months preceding the study. To inform the study, 29 dust samples were taken from 15 agricultural households and 25 samples taken from 13 urban households. The minimum to maximum concentrations in agricultural households were: bifenthrin (0.0-23.9 ng/g); allethrin, two isomers, (0.0-694 ng/g); cypermethrin, four isomers, (0.0-13,500 ng/g); deltamethrin (0.0-5,590 ng/g); esfenvalerate (0.0-66.5 ng/g); imiprothrin (0.0-2,140 ng/g); prallethrin (0.0) and cis-permethrin (45.9-6,300 ng/g); and trans-permethrin (88.4-9,690 ng/g). In the case of the urban households the ranges of reported values were: bifenthrin (0-2,120 ng/g); allethrin, two isomers, (0-289 ng/g); cypermethrin, four isomers, (0-13,100 ng/g); deltamethrin (0-16,300 ng/g); esfenvalerate (0); imiprothrin (0-160ng/g); prallethrin (0-33.6 ng/g); cis-permethrin (11.6-26,700 ng/g): and trans-permethrin (18.4-46,800 ng/g). The most commonly detected compounds in

both sampling sites were: allethrin, cypermethrin and permethrin. Cis- and trans-permethrin were also reported in all homes. Therefore, pyrethroids do persist in and can be detected indoors.

Contaminated Indoor Air: An Indicator of Potential Indoor Pesticide Exposure

The inhalation route of exposure is particularly important to human beings especially in restricted areas where pesticide residues exist (Raeppel et al., 2015).

The PCSTs who volunteered for this study may be exposed to pyrethroids when taking an inventory of chemicals and other equipment in storage areas or if residues exist in the driver's compartment of contaminated vehicles. Items such as equipment and pesticides in the cabs of work trucks are also potential sources of airborne pyrethroids. The six listed pyrethroids of interest to this study are all semi-volatile organic compounds (SVOC) and when airborne can be detected at measureable levels and therefore have the potential for inhalation exposure. They were reported among forty compounds that were detected in indoor air where the concentrations were all above 0.5 ng/m^3 (Yoshida et al., 2004). Luet al. (2013) also found measurable concentrations of pyrethroids in indoor air during a study aimed at determining residential pesticide exposure originating from regular pest control activities prior to the intervention of an integrated pest management

program. 20 samples were taken from households and analyzed for the presence of organophosphates and pyrethroids. When both air and surface samples were considered, pyrethroids were more commonly detected than organophosphates, with concentrations of permethrin and cypermethrin being 2.47 and 3.87 $\mu g/m^{2,}$ respectively, as measured from surface wipes. 5 pyrethroids were found in the air samples, with the highest concentrations for tefluthrin and cyhalothrin at 0.06 ng/m^3 and $0.52ng/m^3$, respectively. Permethrin, allethrin and cypermethrin were all below their detection limits (Lu et al., 2013).

The detection of low concentrations of pyrethroids in air, relative to the concentrations of permethrin and cypermethrin of 2.47 and 3.87 $\mu g/ m^2$ in wipe samples, is not unusual. Low concentrations can be explained by speedy reduction consistent with Barro et al. (2006) who reported the speedy reduction of allethrin and deltamethrin concentration in the air in a test room where aerosol formulations of these active ingredients were dispersed. The rapid breakdown of pyrethroids in air is due in part to a series of photo chemical reactions (Ruzoet al., 1982), some of which yielded products not identified in that report. Barro et al (2006) acknowledged that the low airborne concentrations detected could be due to other factors such as deposition.

Bradman et al., (2007) also reported variations in pyrethroid levels over time, with allethrin, bifenthrin, cypermethrin and permethrin at levels ranging from not detected to 380 $ng/m^{3.}$ They also reported higher concentrations of pyrethroids compared to organophosphates in dust, air and surface wipes samples taken from the interior of farmworker homes (Bradman et al., 2007).

Pyrethroid in the Air of Pest Control Storage Areas

To the best of our knowledge there are no recent studies on the levels of pyrethroids found in the air of commercial pest control storage areas. There is, however, an older study reporting measureable levels of cypermethrin, permethrin and resmethrin in pest control storage buildings (Wright et al., 1996). Data displayed in Table 4 shows that a high level of variability was reported among detected levels, with resmethrin detected at the highest level of $14\mu g/m^3$ in the storage room during the summer when pesticide application usually peaks. The $14\mu g/m^3$ detected in the storage correlated with $5\mu/m^3$ detected in the office of the same pest control company and for the same season.

In general, the high variability in detected levels could be attributed to factors such as chemical and physical properties of individual pesticides (e.g. vapor pressure), spillage, formulation, and transport on the person (Wright & Leidy, 1980; Watt, 2000).

Pyrethroid residues may remain airborne for extended time periods. Under experimental conditions, Leng et al. (2005) showed that while being variable, pyrethroid residues sometimes remain for periods of months after indoor application. Concentrations of cyfluthrin, permethrin, deltamethrin, and cypermethrin were measured at 1 day, 4-6 months and 10-12 months post application. At 1 day post application, median cyfluthrin concentration was $4.9ng/m^3$ while at 4-6 months two locations had 7.7 and 3.6 ng/m^3. No cyfluthrin was detected after that. At 1day after cypermethrin was applied, the concentration was $45ng/m^3$, but was already below the detection limit within 4-6 months. At 1 day post application, the median deltamethrin concentration was $20.8ng/m^3$.

However, none was subsequently detected. In the case of permethrin, a concentration of 18.1 ng/m^3 was detected in one building at one day post application, while the median concentration declined to 8.9 ng/ m^3 and 4.9ng/m^3 at 4-6 and 10-12 months, respectively (Leng et al., 2005).

The fact that pyrethroids are semi-volatile organic compounds could play a role in determining their concentration in air following their release into the environment. As such, quantities which are found in air could originate from dust within the same building, as dust acts as a repository from which re-volatilization could occur (Butte & Heinzow, 2002). Both thermal desorption and re-suspension could also give rise to an airborne concentration of pyrethroids (Elflein et al., 2003; Butte & Heinzow, 2002).

In addition to indoor dust, personal protective equipment, tools and pesticide containers within an enclosed space (building or vehicle) could also be sources of airborne pyrethroids. Therefore, levels of airborne pyrethroids, which are detected within an enclosed space such as a pesticide storage area or facility, may also vary over time.

Table 4: Pyrethroids detected in $\mu g/m^3$ in the ambient air of insecticide storage rooms of commercial buildings in a 2 hour period during summer and winter [abc] compiled from (Wright et al.; 1996).

Company	Cypermethrin				Permethrin				Resmethrin			
	Office and insecticide storage room in same buildings				Office and insecticide storage room in same buildings				Office and insecticide storage room in same buildings			
	Summer		Winter		Summer		Winter		summer		Winter	
	O	S	O	S	O	S	O	S	O	S	O	S
A	NP	NP	NP	NP	0.2	2.34	0.05	<0.01	NP	NP	NP	NP
B	NP	NP	NP	NP	NP	NP	NP	NP	0.59	<0.01	<0.01	<0.01
C	NP	NP	NP	NP	NP	NP	NP	NP	NP	NP	NP	NP
D	1.2	11.66	P	P	1.94	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
E	2.4	4.15	P	0.02	NP	NP	NP	NP	NP	NP	NP	NP
					Office and insecticide storage room in different buildings				Office and insecticide storage room in different buildings			
F	0.16	2.82	P	0.47	NP	NP	NP	NP	0.31	<0.01	<0.01	<0.01
G	NP	NP	NP	NP	NP	NP	NP	NP	0.63	<0.01	<0.01	<0.01
H	NP	NP	NP	NP	NP	NP	0.03[d]	NP	2.18	<0.01	<0.01	<0.01
I	P	P	P	P	NP	NP	NP	NP	5.22	14.1	<0.01	<0.01
J	<0.01	<0.01	0.01	0.02	NP	NP	NP	NP	1.09	0.01	<0.01	<0.01

[a]Abridged table, in the original 260 pesticide samples were available for analysis of which 28 were for Resmethrin, 20 for Cypermethrin and 10 for Permethrin. On the whole more ($p = 0.05$) insecticide were found in storage than in offices when the samples were combined. There was no difference in levels in the rooms irrespective of whether insecticide storage was in the same or different building. [b] O = office room S= insecticide storage room [c] Insecticide not present in the insecticide storage room or above the detectable limit in air [d] Insecticide not in inventory of insecticide storage room but was present in the ambient air of storage room or office.

Pyrethroids in Socks Worn by Pest Control Service Technicians

Some pyrethroid insecticides require the wearing of socks as a precautionary measure to reduce hazards to humans (CSI, 2014). The label for Cyper TC Insecticide, which contains cypermethrin requires applicators to wear chemical resistant footwear and socks as components of their Personal Protective Equipment (PPE) (CSI, 2014). It has been demonstrated that PPE is effective in guarding against dermal exposure of pest control operators (PCO) whose jobs involved mixing/loading and applying chlorpyrifos (Van Der Jagt et al., 2004). One component of the study involved baseline (pre intervention) and post intervention measurements in order to compare the effectiveness of safety shoes in preventing exposure to ankles and lower legs. Intervention also included viewing an instructional video on the proper use of PPEs. Actual dermal exposure to ankles was ascertained by measuring residues of chlorpyrifos found in 5.5cm x 5.5cm, cotton pads that were taped to the PCO's ankles. Actual dermal concentration to the ankle was determined by relating the concentration in the pad to standard anatomical dimensions. Actual baseline dermal exposure to the ankle in ng/cm^2 had an arithmetic mean of 0.5 and a range of 0.02-7, whereas the post intervention arithmetic mean was 0.02 and a range of 0.02-0.04 (Van Der Jagt et al., 2004). 12 pre intervention samples were below detection, while 13 post intervention samples were below detection.

The reported concentrations of chlorpyrifos residues in the cotton pads worn around the ankle suggest that measurable quantities of pesticides can be conveyed to and retained by socks even when chemical- proof boots are worn. Therefore, socks that protect ankles during pesticide application can be a vehicle for take- home pyrethroid exposure.

Take-Home Pesticide Exposure

While there are numerous studies that illustrate the importance of take-home pathways to pesticides exposure, as far as we are aware, there is none that is specific to either pyrethroids or pest control service technicians. This indicates a need for the current study. Fenske et al.'s (2000) research over an eight-year period was aimed at understanding the potential health risks to children due to pesticide exposure originating in an agricultural area where their parents worked. The study showed that children of farm workers were at a greater risk when compared to those in a control group. While some findings of pesticides in the homes were attributed to their residential proximity to farms, others credited take -home exposure to parents' occupation (Fenske et al., 2000). In addition, when both soil and house dust was tested, there were greater concentrations of organophosphate pesticides in house dust than in soil. This discovery, therefore, suggests that organophasphates were being transported into the house environment from agricultural areas (either via transfer of contaminated agricultural dust/soil or from contaminated clothing or PPE).

When comparing take-home exposure with exposure due to distance from farms among agricultural and non-agricultural families, Fenske et al.(2000) found that agricultural families that lived farther away from farms had greater concentrations of OPs in both urine and dust samples. There was also an ongoing exposure risk in children belonging to agricultural families with fluxes in concentrations depending upon the seasonality of pesticide applications (Fenske et al., 2000)

In another study, Lozier et al. (2012) investigated temporal residential atrazine concentration in the homes of commercial pesticide applicators. Dust samples were

collected in the applicators' homes during peak pesticide application periods (1st visit) and in non-peak periods (2nd visit). Dust samples from entryways, master bedrooms, living rooms and kitchens were analyzed for atrazine. Concentration was also converted to reflect actual loading in ng/cm^2. The highest loadings were detected in entryways during the 1st visit, followed by entryways in the 2nd visit. After entryways, loadings decreased from kitchens to master bedrooms and to living rooms. All values in the 1st visit were higher than in the 2nd visits (Lozier et al., 2012). In addition, atrazine loads in homes were affected by where the applicators changed their work clothes and shoes and performed their hygiene practices. Therefore, the use of PPEs could break the take home exposure pathway. Lozier et al. (2012) not only documented the existence of take-home exposure, but also that take-home exposure correlates with changes with the occupational use of a pesticide.

The potential for take-home exposure to pesticides has been further substantiated as indicated in Table 5. Table 5 displays the percentages of child and adult urine samples that had levels of organophosphate metabolites and of house and vehicle dust samples that had levels of organophosphates above the limits of quantitation LOQ.

The presence of measurable levels of these pesticides in vehicle and house dust suggests the existence of a take-home exposure pathway. The presence of metabolites in children's urine samples further supports this hypothesis since the exposure of children who do not work in agriculture is most likely conveyed by their parents (Thompson et al., 2003).

Table 5: Percent of child and adult urine samples with levels above the LOQ and of house and vehicle dust samples with levels above the LOQ in a study of take-home exposure pathway of organophosphates.

	Child	Adult	House dust#@	Vehicle dust**
Compound	N211	N213	N 156	N190
Urine				
Percent above LOQ*				
MPD	19	20		
DMTP	88	92		
DMDTP	44	54		
DEP	0.9	0		
DETP	37	48		
Dust				
Percent above LOQ*				
Azinphosmethyl			85	87
Malathion			15	16
M-Parathion			13	12
Phosmet			14	22
Chlorpyrifos			26	18
Diazinon			3.8	2.1

Compiled from Thompson et al., (2003); *Percentage of all samples; # Limits of quantitation (µg/L) for urine are: DMP=7.4; DMTP=1.1; DMDTP= 0.6; DEP=2.9; DETP=1.3; @ Limits of quantitation (µg/L) for house dust are: azinphosmethyl= 0.09; Malathion=0.16; m-parathion= 0.12; phosmet= 0.13; chlorpyrifos=0.15; diazinon 0.17; ** Limits of quantitation (µg/L) for vehicle dust are:azinphosmethyl= 0.11; Malathion=0.08; m-parathion=12; phosmet= 0.09; chlorpyrifos=0.11; diazinon 0.11; DMP = dimethylphosphate, DMTP =dimethylthiophosphate, DEP = diethylphosphate;DETP=diethylthiophosphate

PPE, Worker Hygiene and Occupational/Take-Home Pesticide Exposure

Workers who practice improper use of PPE and improper hygiene create a greater potential for take-home exposure. Curl et al. (2002) demonstrated that contaminated clothing and skin are sources of pesticide residues in commuter vehicles, which further convey these contaminants from the work place of agricultural workers to their homes.

As such, workers who are exposed to higher loadings of the selected pyrethroids have a greater potential for take-home exposure by increasing loadings in the driver compartment of service and personal vehicles.

When custom-fitted PPE with chemical resistant boots, respirators, gloves and hoods were properly used, they were found to be effective in protecting pest control operators from exposure to chlorpyrifos (Van der Jagt et al., 2004). In that study, the arithmetic mean lower leg exposure to chlorpyrifos in ng/cm^2 prior to the use of PPE was 5.6 and the range was 0.03- 24.2. These values were reduced to a mean of 3.4 and a range of 0.03-17.2 when protective boots were worn. At the same time, the mean exposure to ankles prior to intervention was 0.5 with a range of 0.02-7. In this case, the mean was reduced to 0.02 and the range was lowered to 0.02-0.04 when protective boots were worn. Both results demonstrate the effectiveness of chemical resistant boots in reducing pesticide exposure (Van Der Jagt et al., 2004).

In another study, cotton socks were used as an exposure matrix in risk assessment among four pesticide applicators who applied the insecticide acetamiprid in an apple orchard (Kim et al., 2013). Dermal exposure of legs and feet varied from 1-102.9 mLh^{-1} (Table 6). This not only shows the usefulness of socks as an exposure matrix, but also as a useful component of PPE. It follows, however, that when pesticide applicators change these items in their homes, the result can be take-home exposure (Lozier et al., 2012).

Table 6: Dermal exposure ($mL.h^{-1}$) to acetamiprid in an apple orchard during application.

Body Part	Operator 1	Operator 2	Operator 3	Operator 4	average
Left lower leg	102.9	65	42.7	52.6	65.8
Right lower leg	75.9	66.2	54.1	35.5	57.9
Feet	4.1	1	1.9	1.2	2.11
Total	182.9	132.2	98.7	89.3	125.8

Compiled from Kim et al. (2013)

Under these experimental conditions, cotton socks covering the operators' lower legs and feet were contaminated at the total rate of 125.8 $mL.h^{-1}$ Table 6 shows that a substantial quantity of pesticide can be added to PPEs during pesticide application. Therefore, if pesticide applicators removed and stored these PPE in designated locations prior to arriving home, the take-home pesticide exposure pathway can be broken or the quantities of pesticides taken home reduced. Bradman et al. (2009) postulated that in exposure scenarios, pesticides may adhere to the clothing, body or shoes worn by applicators. Pesticides that adhere to workers' body, clothing or shoes also create a potential for take home exposure. This can be the case when these items are not removed or when washing is not done before workers go home.

In an intervention study aimed at reducing malathion occupational and take-home exposure, Bradman et al. (2009) demonstrated that exposure could be avoided by wearing gloves, by removing contaminated work clothes, and by hand washing, among other hygiene practices prior to commuting home. The use of disposable gloves resulted in lower malathion loadings among those who wore gloves when compared to those who did not. Those who wore disposable gloves had a median concentration of 8.2 μg per pair while those who did not had a concentration of 777.2 μg per pair, respectively ($p<0.001$).

A lesser amount of the main malathion metabolite was also found in the urine of those who wore gloves compared to those who did not, 45.3 μg/g vs. 131.2 μg/g ($p < 0.05$). Therefore, good hygiene practice and the proper use of protective gear have been shown to reduce pesticide exposure (Bradman et al., 2009).

Lozier et al. (2012) further demonstrated that personal protective equipment and hygiene practices can break the take-home exposure pathway. Their findings showed that homes where pesticide applicators changed their work shoes, an item of PPE, had significantly higher levels of atrazine contamination when compared to homes where applicators had changed their work shoes at work sites. Removing shoes before going into homes was correlated with lower loads of atrazine ($p=0.03$), while removing work clothes in the master bedroom resulted in significantly ($p=0.01$) greater loads in these areas (Lozier et al., 2012).

Pesticide Exposure as a Function of Training

There is an increased risk of pesticide exposure whenever applicators ignore basic instructions relating to the proper use of such chemicals. This is especially true if fundamental safety precautions such as safe and effective use of PPEs, sanitation and worker hygiene are not being taught or are ignored (Damalas & Eleftherohorinos, 2011). On the other hand, training in the safe use of pesticides can reduce both occupational and take-home exposure. As such, both certified pest control operators (CPO) and pest control service technicians (PCSTs) must meet specific training and certification requirements before they are deemed qualified to apply pesticides safely.

The Florida Department of Agriculture and Consumer Services and the Division of Agricultural Environmental Services administer regulations which address the safety training of CPOs and PCSTs. The relevant regulation (Florida Statutes Title XXXII, Chapter 482) specifies that CPO certification is awarded only to a person who has passed the qualifying examination and is therefore certifiable regarding safety of persons and property. For annual recertification CPOs must address the precautions necessary to safeguard life and health while practicing pest control and to demonstrate their ability to read and understand pesticide labels (Florida Statutes, Ch. 482.111(10) (a) 2 and 5).

Additionally, the PCSTs must operate under the direct supervision of CPOs. (Chapter 482.091(2) (a) of the Florida Statutes states that PCSTs must consult with the CPO regularly regarding safe and proper use of pesticides. Also, Chapter 482 091.(2)(e)(10) specifies that "each identification card holder must receive 4 hours of classroom training in pesticide safety . . . within 6 months after issuance of the card or must have received such training within 2 years before issuance of the card." Given this level of specificity in the Florida Statutes, the proper use of personal protective equipment is clearly an important aspect of the safe use of pesticides. Indeed, Van Ger Jagt et al. (2004) demonstrated that when PCOs received this type of training before applying chlorpyrifos, the arithmetic mean dermal exposure to the ankle was reduced from 0.5 ng/cm^2 to 0.02 ng/cm^2.

CHAPTER 3 – RESEARCH PROJECT

Introduction

To address the lack of available information on the potential exposure of Florida pest control technicians to pesticides and the potential for take-home exposure among family members, we implemented a project in the Tampa Bay area focused on pyrethroids, the most commonly applied insecticide in the state. In considering exposure routes for applicators, an important parameter is exposure time. Applicators spend a considerable fraction of their work time traveling to and from applications, sites in work vehicles (which can in some cases also be their private vehicles) and in storage depots/sheds. This means that applicators can be exposed to pesticides they use in their line of work in these environments, both via inhalation of air and contaminated dust particles. These micro-environments also contain work equipment that may be contaminated and thus serve as sources of pesticide exposure to applicators.

Therefore, our research plan focused on measuring levels of selected pyrethroids in the air and dust of storage depots/sheds and in work/personal vehicles. We also decided to measure levels in socks worn by applicators so as to estimate the potential for take-home exposure via transfer of pesticides in work clothing.

Methodology

Subject Recruitment. We targeted 11 pest control companies to recruit a cohort of volunteers to participate in this study. We attempted to balance representation from smaller and larger operations in order to ascertain different take-home exposure profiles in workers from these different types of applicators. Companies were contacted by telephone and/or walk-in visits. Following this, an introduction of the project was done by a letter and verbal conversations. Although the 11 companies were targeted due to their owners or managers having previously expressed an interest in participating, ultimately only 4 companies actually agreed to participate. Three companies are large operators with 4-10 employees and one was small having less than 4 employees.

The certified operators in charge of the companies gave consent and recommended service technicians and service vehicles for testing. A total of five technicians were available to participate in the study, all of whom were given a project briefing. Only two of these technicians had personal vehicles that could be made available for testing, but four were willing to donate their socks for testing and only the larger three companies had chemical storage areas for testing. Ultimately, we were allowed access to three pesticide storage areas of commercial pesticide applicators, five service vehicles and two personal vehicles which were used by pest control service technicians. In addition, four volunteers agreed to provide a pair of socks for testing. Absolute care was taken to ensure that participants understood that there would be no identifying information of any company or individual made available.

While the sample size in the study is less than ideal to make statistical analyses, due to the timeframe available to complete the project, we decided to pursue the project with what was available. We reasoned that the results, while limited in extent to which results could be extrapolated, would nonetheless provide initial results to determine whether or not further studies would be warranted.

Questionnaire. At the time of the sampling, we conducted a survey of the participating pest control service technician. The intent was to determine the level of training, experience on the job, and hygiene and personal protective equipment usage practices The questionnaire used in the survey was qualitatively and quantitatively analyzed and is included as Appendix A.

Targeted Pyrethroids. The six targeted active ingredients in Table 1 are pyrethroid compounds registered for use in Florida's pest control industry. They are also expected to be present in the work environment of PCSTs as can be inferred from the results of the personal survey and from the reports of chemical suppliers in the areas where the pest control companies operate.

Chemicals and Standard Materials. The standard materials used for the determination of pyrethroids are listed in Table 7. 1mL each of the solutions of allethrin, bifenthrin, cyfluthrin, cypermethrin, deltamethrin and permethrin at concentrations of 1mg/mL was purchased from Crescent Chemical Company. Each was emptied into a 10mL volumetric flask, a few drops of toluene were added to ensure complete dilution,

and diluted with iso-octane to make a final volume of 10 mL at a concentration of 100ppm (stock solutions).

Table 7: Pyrethroid standards used in this study.

Product Description	Component	Cat #	Solvent	CAS #	% Purity	Gravi-metric	Analyte (µl/mL
Allethrin Solution	Allethrin*	7008M.10	Methanol	584-79-2	96.5	1036	1000
Bifenthrin solution	Bifenthrin	8330M.10	Methanol	82657-04-3	98.5	1001	986
Cyfluthrin Solution	Cyfluthrin^	8325EA.10	Ethyl Acetate	6835937-5	98.5	1003	988
Cypermethrin Solution	Cypermethrin	7307EA.10	Ethyl Acetate	52315-07-8	99.5	1001	996
Deltamethrin Solution	Deltamethrin	8343EA.10	Ethyl Acetate	52918-63-5	99.9	1003	1002
Permethrin solution	Permethrin	7915EA.10	Ethyl Acetate	52645-53-	99.9	1003	1002
trans-Cypermethrin D6	Dimethyl D6#	XA1189040 0AC	Acetone	82523-65-7	98.5	-	-

^ Mixture of four isomers 23%, 34.9%, 19.5% & 22.5%; # Isotopic purity 99% chemical purity 99.5% mixture of c(R (cyano)1R3S/S(cyano)1S3R) and D(R(cyano)1S3R/S(cyano)1R3S; compile from Certificate of Product data (Crescent Chemical Co.)

Trans-Cypermethrin D6 at 100 ng/µL was diluted to 10 ppm. Dichloromethane (DCM), hexanes, acetone and toluene were all pesticide grade and purchased from Fisher. Other materials, including silica gel and anhydrous sodium sulfate, were also purchased from Fisher.

Mixed Pyrethroid Stock Solutions. To prepare a 10 ppm pyrethroid mixed stock solution 1mL each of allethrin, bifenthrin, cyfluthrin, cypermethrin, deltamethrin and permethrin standard solutions at a concentration of 100ppm, prepared as described previously was added to a 10 mL volumetric flask and isooctane added to make a final

volume of 10 mL. With d_6 trans cypermethrin and the pyrethroid mix now at the same concentration of 10 ppm, we prepare a 1 ppm pyrethroid and d_6 trans cypermethrin mix by adding 1mL of each to a 10 mL volumetric flask and further adding isooctane to make a final volume of 10 mL. The mixed pyrethroids and d_6 trans cypermethrin stock solution at 1ppm was then placed in an amber glass vial, capped and sealed with teflon and then stored in a freezer until used.

Calibration Standard Solutions. The mixed pyrethroid solution was diluted in isooctane to concentrations of 800, 400, 200, 100, 50, 20, 10, 5 and 1 ppb. The points from 800 to 50 ppb were used to make a five point calibration curve for quantitation of higher concentrations of analyte and points from 50 to 1 ppb were used to make a calibration curve for quantitation of lower concentrations of analytes. A chromatogram of the pyrethroids mix at the 1 ppb concentration is given in Figure 3 showing its adequacy to quantify concentrations of analyte beginning at that lower end of the concentration range.

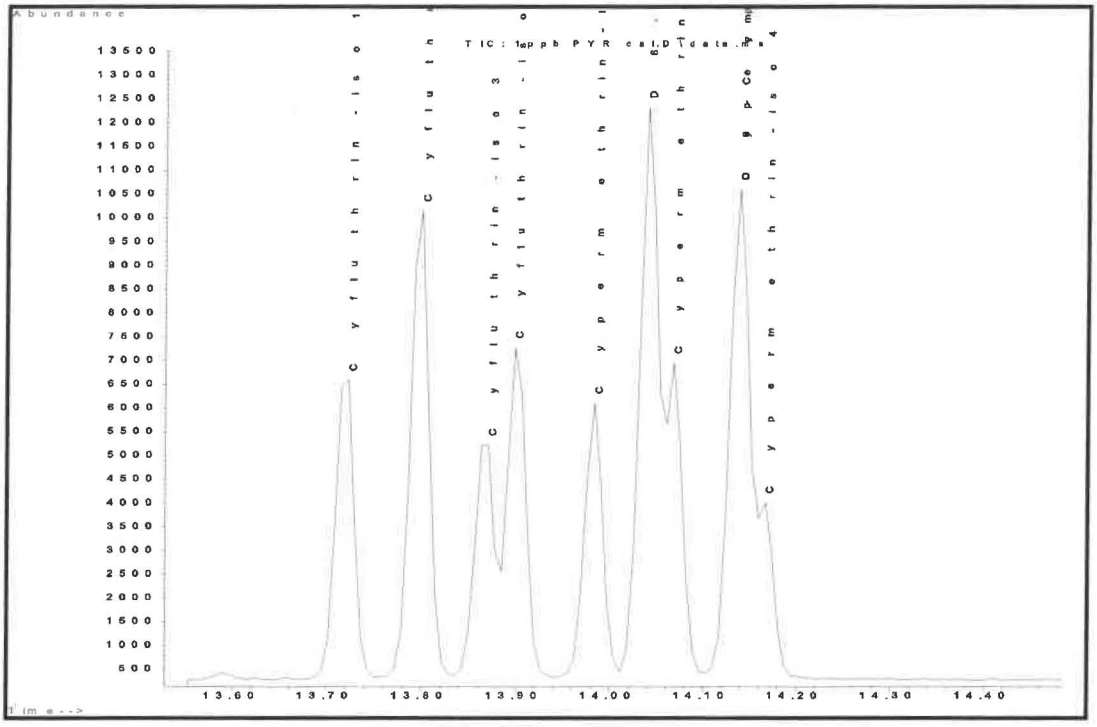


Figure 3: Chromatogram of the pyrethroid mix and d_6-cypermethrin at 1ppb

Sample Collection

Air Sampling. Circular polyurethane foam (PUF) plugs were cut to dimensions of 22 mm diameter sized to fit snugly into 20 mm diameter glass sampling cassettes and approximately 7.6 cm in length. These were cleaned by successive Soxhlet extractions overnight (minimum 16 h) with pesticide grade dichloromethane, then hexane. The PUF disks were placed in aluminum foil, air dried in a desiccator and subsequently stored in amber glass vials until installation in cassettes prior to air sampling.

Air was collected from three pesticide storage areas, five service vehicles and 2 personal vehicles used in commuting to and from work. Sampling was done during the Fall of 2013 and late Summer of 2014. An Aircheck Universal Pump, Model 224 43XR (SKC) and a Gilian GilAir plus 5 Personal air sampling pump (PASP) were used for air sampling. Teflon tubing was used to connect the PASP to a Glass Holder (Supleco Solutions) outfitted with the 22 mm PUF Plug. Teflon was also used to securely wrap the connections to make them air tight. The Aircheck Universal Pump, Model 224 43XR (SKC)) and a Gilian GilAir 5 Personal air sampling pumps were set to sample air at a flow rate of 5 L/min and 3 L/min, respectively. Aluminum foil was used to cover the sampling cassettes to reduce degradation of pyrethroids exposed to light.

During air sampling of personal and service vehicles, the sampling apparatus was mounted or hung within the breathing zone of drivers. In sampling the storage areas, however, the air sampling apparatuses were mounted on tripods within 1-1.5 meters from the floor in the middle of the room. After the sampling period, the PUF plugs were removed from the glass holder and placed in pre-cleaned glass vials. They were then wrapped in aluminum foil and transported on dry ice in a cooler back to the laboratory and stored in a freezer until extraction. The volumes of air collected amongst the locations sampled varied between 0.744 m^3 and 1.6823 m^3, depending mainly on the amount of time the pest control technicians had available to accommodate the researcher (sampling was carried out during normal working times and conditions). Figure 4 shows details of the sampling setup.

Dust Sampling. Dust samples were collected at the pesticide storage areas and from service and personal vehicles used by the technicians. The samples were collected by using a ShopVac Hangup portable, 2.5Gal.U.S. (Shop*vac Corporation, Williamsport, PA) to which a new Vacuum Dust Collector model ZA0059 (Zeflon International, Inc. 5350 Space SW 1st Lane Ocala, Florida) was connected to the standard 1¼ inches vacuum hose for the collection of each sample. A new vacuum dust collector was attached after each sample to prevent cross contamination of the samples as can be seen in Figure.3. The vacuum dust collector was filled a maximum of two times when dust was easily available at collection points.

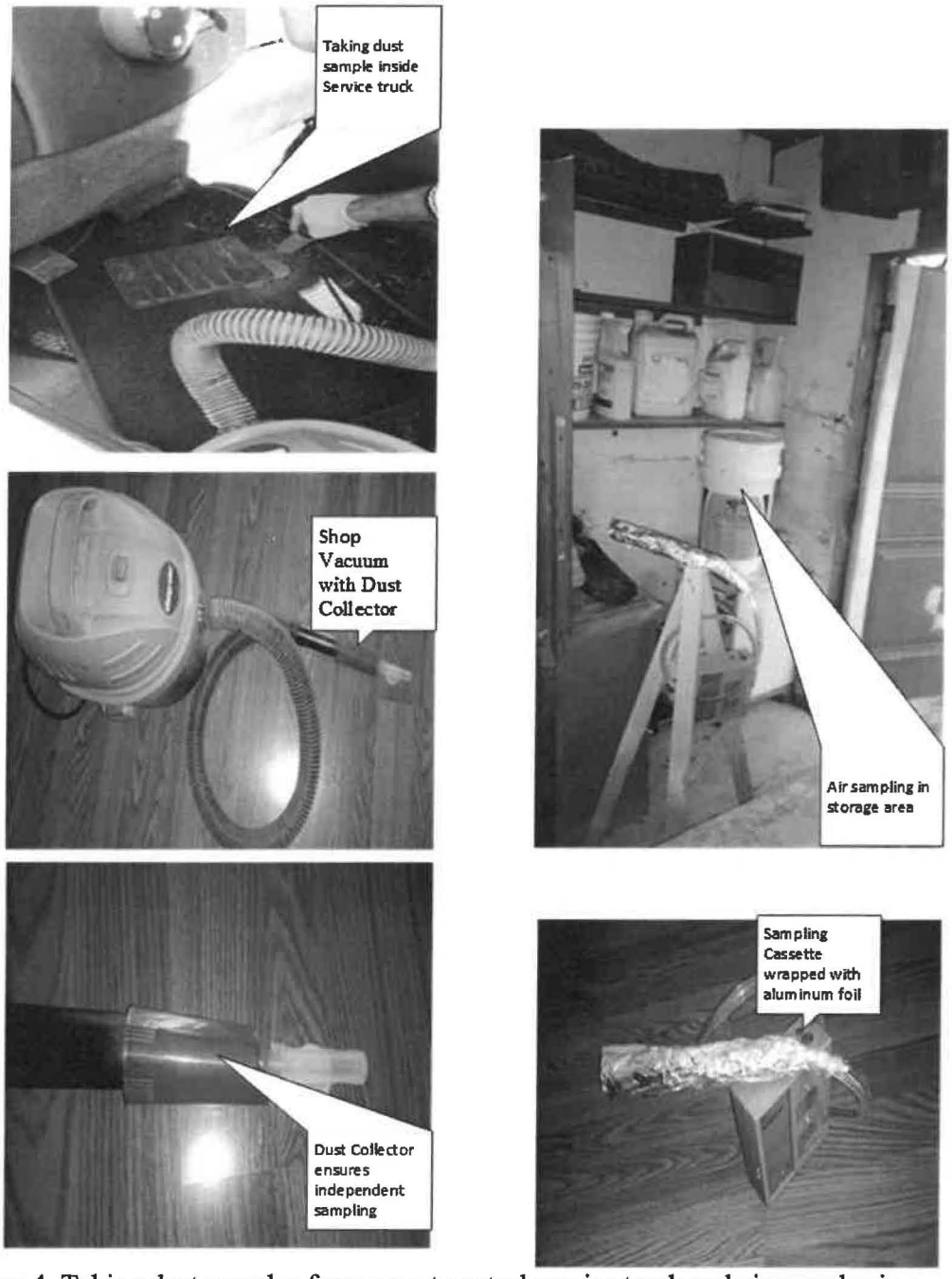


Figure 4. Taking dust samples from a pest control service truck and air samples in a storage area and sampling set up.

The vacuuming time did not exceed five minutes, with the quantities of dust varying from 2.1908 grams to 15.6979 grams. Subsequent to sample collection, the dust collector was emptied into a pre-cleaned glass vial and capped and wrapped in aluminum foil. It was then placed in a cooler on dry ice and transported to the laboratory and stored in a freezer. Prior to extraction, tweezers were used to remove macro-particles and any particle which seemed to be of organic origin. Dust samples collected in the Fall of 2013 were extracted within 3 months of collection, while those collected in late Summer of 2014 were extracted within 2 months of collection.

Socks Sampling. Four pairs of socks were collected in each sampling period providing a total of eight pairs of socks, one volunteer withdrew from the study. Two pairs of collected socks during the Fall sampling period were worn for two work days whereas the others were worn just once. These were wrapped in aluminum foil and placed in Ziploc bags and transported and stored in similar fashion as the other samples.

Extraction

Air Samples. The PUF plugs were removed from the freezer and cut into small pieces using a stainless steel pair of scissors. They were then placed in a 50 mL beaker and covered with approximately 30 mL of 1:1 dichloromethane (DCM): hexane mixture. These were then covered with aluminum foil and ultra-sonicated for 30 minutes in a VWR Scientific Aquasonic Ultrasonic Water Bath, Model 750D. The solvent was decanted into a beaker. The extraction was repeated twice successively.

The combined extracts were filtered through glass wool and concentrated to 1mL using a Buschi Rotavapor R-210 with a Heating Bath B491 and a Thermo Scientific NESLAB Thermoflex™ Recirculating Chiller, followed with a gentle stream of nitrogen via a N-EVAP 111 Nitrogen Evaporator. The concentrated extracts were solvent exchanged into iso-octane by the addition of 1mL of iso-octane to the concentrated extracts in 1:1 DCM: Hexane mixture and again concentrated with a gentle stream of nitrogen to 1mL. The concentrated extracts now in iso-octane were placed into chromatography vials and stored until analyzed a year later.

Dust Samples. The weighed dust samples were placed in glass centrifuge tubes and 15 mL of a solution of 1:1 hexane: DCM added and ultrasonicated for 30 minutes similar to the PUF plugs. Each tube was, however, ultracentrifuged in a Fischer Scientific Centrifuge, Model 225 for 2 minutes and the supernatant placed in a round-bottom flask. Each dust sample was extracted two more times as previously done and the combined extracts were placed in the round-bottom flask. Each sample was concentrated to approximately 1 mL using a rotary evaporator and a gentle stream of nitrogen and solvent-exchanged with isooctane similar to the PUF plugs. The dust samples were subsequently cleaned up with a silica gel mini-column.

Socks Samples. The socks were cut up into small pieces using a pair of stainless steel scissors and extracted and filtered similar to the PUF plugs which were used for air sampling. They were then concentrated using the same equipment that was used with the PUF plugs. They were extracted and solvent exchanged into isooctane. Like the dust samples, these were cleaned up via a similar column.

Sample Clean Up

The concentrated dust extract was cleaned by eluting through a silica gel chromatography column. The column was prepared by plugging a Specialty Glass Column, SUPELCO 64747, with glass wool. One (1) gram of silica gel was quickly added followed by a centimeter of anhydrous sodium sulfate. The column was immediately pre-eluted with 5 mL DCM followed by 5 mL of hexane. The concentrated extract in iso-octane was then added to the column and eluted with 10 mL of DCM/hexane (3:7) followed by 10 mL DCM. Each eluate was collected in a separate centrifuge tube and concentrated using a gentle stream of nitrogen, solvent-exchanged into iso-octane and concentrated to a final volume of 1 mL.

The concentrated socks extracts in iso-octane were cleaned up using the silica gel column as was the case with the PUF plugs extracts, except that the amount of silica gel varied between 1 to 3 grams (depending on the amount of dye in the socks). The extracts varied in color and consistency because of the amount of dye present in the socks extract. Elution was done with 10mL of DCM: Hexane 3:7 followed by 10mL of hexane. The eluate from each sample was collected in centrifuge tubes, concentrated to 1mL, and solvent exchanged into iso-octane similar to the dust samples. Each concentrated extract, now in iso-octane, was finally blown down with a gentle stream of nitrogen to a final volume of 1mL then placed in chromatography vials and stored in a freezer until analyzed.

Analysis

Samples were analyzed via gas chromatography negative chemical ionization mass spectrometry (GC-NCI- MS) using an Agilent 7890A gas chromatograph coupled to an Agilent 5975C inert XL EI /CI MSD (mass selective detector) with Triple- Axis Detector and an Agilent7693 Autosampler. The column was an Agilent 19091S-433:325° C: 30 m x 250μm x 0.25μm and the carrier gas was helium with a constant flow of 1.1μL per minute.

The MSD was initially operated in the scan mode in order to determine the range of retention times and masses of the compounds subsequent to which selective ion monitoring (SIM) was done in the negative chemical ionization (NCI) mode using methane as the reagent gas. The ions monitored, limit of detection and retention times of the pyrethroid compounds and the pyrethroid surrogate are given in Table 8. Consistent with a method which was previously used by Roa et al. (2010), the temperature program was: an initial temperature of 100°C which was held for 1 minute, ramped to 230°C at a rate of 15 °C per minute, ramped to 310 °C at a rate of 10°C per minute and finally held for 2 minutes. Using splitless injection mode, the injection volume was 3μL.The MSD transfer line temperature was 280°C and the inlet temperature was 275°C. The solvent delay time was set to 3 minutes. Quantification was done using the five-point calibration described previously for each target pyrethroid using the instrument's Chemstation software.

Quality Control

Breakthrough Analysis during Air Sampling. Since sampling was done at 3 L/min and 5L/min, we also determined the breakthrough of pyrethroid during air sampling at these two flow rates. PUF plugs, similar to those used in air sampling, were installed into two glass holders which were then mounted on top of each other to make a two layer sampling train. The junction between each layer was made airtight by wrapping securely with teflon and the completed sampling train was wrapped with aluminum foil. The sampling train was connected to the PASP in the manner previously described and mounted onto a laboratory clamp. Trans-cypermethrin (100μL at 10 ppm) was spiked into the first layer of each sampling train and allowed to equilibrate for 30 minutes. This was repeated three times for a sampling rate of 3L/min and three times for a sampling rate of 5L/min. Following equilibration, the pumps were turned on, and air volume of 0.8357, 0.7352 and 0.8324 m^3 and 0.8267,0.6735 and 0.7942 m^3 allowed to flow through the 3L/min and 5L/min sampling train, respectively. The PUF plugs were immediately extracted and subsequently analyzed in accordance with the methods used in this study. The breakthough of d_6 trans- cypermethrin was used as a proxy of the breakthrough of pyrethroid during air sampling. Breakthrough percentages were calculated and the average for air collected at both 3L/min and 5L/min was 4 %. Therefore, there was no need to correct for breakthrough.

Table 8: Ions monitored and retention times of target pyrethroids and surrogate solution.

PK#	Compound	QIon	Exp_RT
1	Allethrin	167	9.434
2	Bifenthrin	386	11.835
3	cis-Permethrin	207	13.213
4	trans-Permethrin	207	13.321
5	Cyfluthrin-iso1	207	13.722
6	Cyfluthrin-iso2	207	13.8
7	Cyfluthrin-iso3	207	13.863
8	Cyfluthrin-iso4	207	13.899
9	Cypermethrin-iso1	207	13.983
10	D6-Cypermehtin-Iso1	213	14.04
11	D6-Cypermethrin-Iso2	213	14.138
12	Cypermethrin-iso2	207	14.068
13	Cypermethrin-iso3	207	14.138
14	Cypermethrin-iso4	207	14.166
15	Deltamethrin	297	15.428

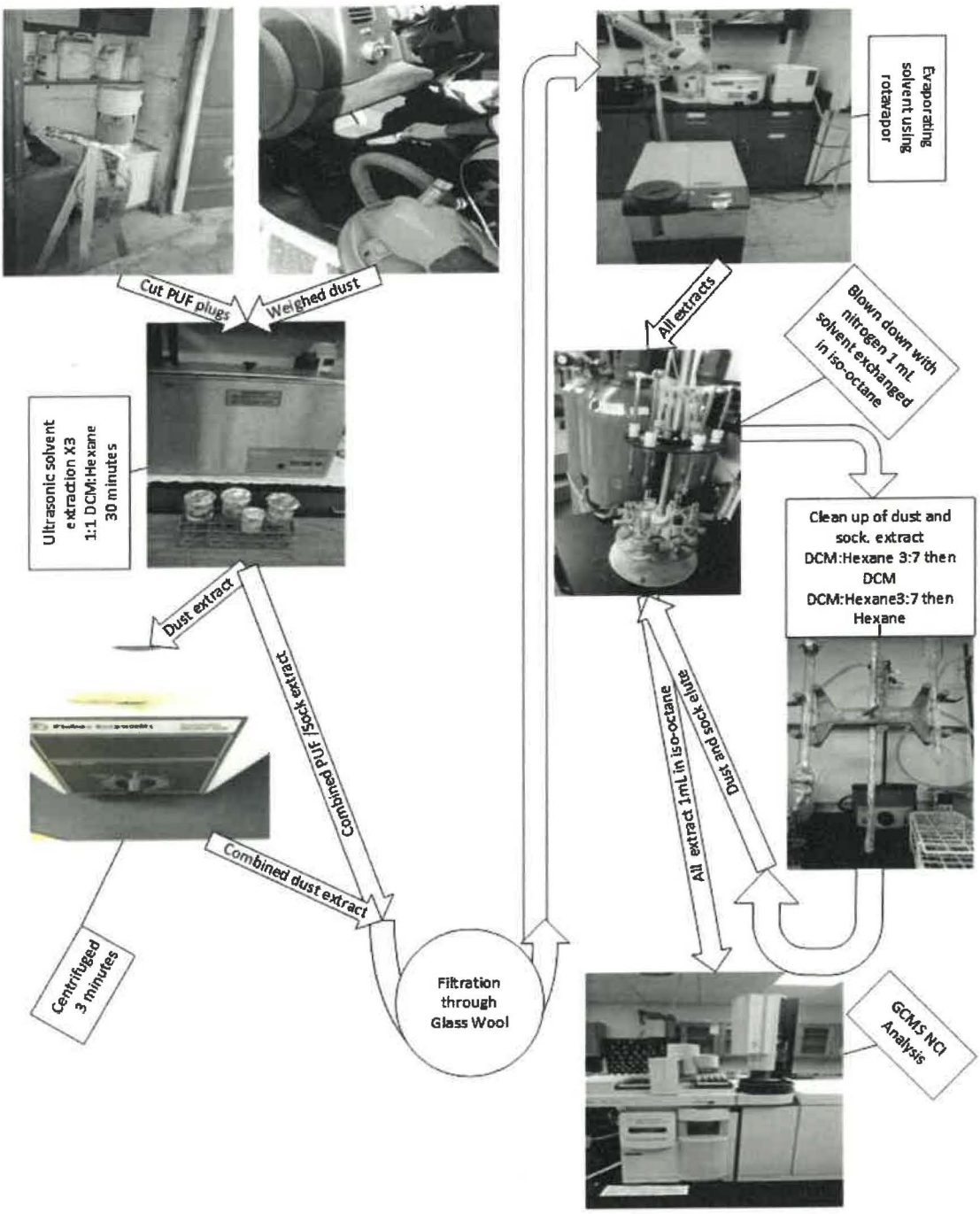


Figure 5: Dust, air and sock sample extraction and preparation.

Percentage Recovery of Pyrethroid From Dust, PUF Plugs and Socks

Samples: The percent recovery of pyrethroids from dust, PUF plugs and socks samples was determined by spiking 3 samples of each of these matrices with trans – Cypermethrin d6 (100µL, 10ppm), allowing 30 minutes for equilibration and extracting them consistent with the methods in this study. Percentage recoveries are presented in Table 9. The actual quantities of each pyrethroid in the samples were determined by adjusting the determined values to account for the unrecovered percentages of trans –cypermethrin d6.

Table 9: Percent recovery and breakthrough.

Matrix	Ave Percent Recovery	Percent Breakthrough
Air Flow Rate of 3L/min	66.	4
Air Flow Rate of 5L/min	42	4
Dust Recovery	43	
Socks extracted	40	

CHAPTER 4 – RESULTS AND DISCUSSION

Survey of Participating Technicians

Before physical data collection, a questionnaire was distributed to volunteers to determine their levels of experience and training and certain hygiene practices which can highlight how well they follow the advice and/or regulations that they learned during training. Table 10 below summarizes the results of the survey.

Table 10: Summary of responses to questionnaire.

Item	Tech A1	Tech A2	Tech B	Tech C	Tech D
Length of time at work (mo)	0-6	>24	>24	12-24	12-24
Training in safe use of pesticides	Y	Y	Y	Y	Y
Storage of work clothes	With regular laundry	With regular laundry	With regular laundry	With regular laundry	Designated basket away from regular laundry
Frequency with which work socks are changed	Mostly daily	Mostly daily	Mostly daily	Mostly daily	Always daily
Frequency with which work pants and shirts are changed	Mostly daily	Mostly daily	Mostly daily	Mostly daily	Always daily
Use of chemical resistant footwear	Never	Sometimes	Scarcely	Never	Always
Frequency with which work footwear is changed before going home	Never	Sometimes	Scarcely	Never	Always
Frequency with which tech reported having to go to pesticide storage in work day	Scarcely	Always	Sometimes	Sometimes	Always

With regard to experience, two technicians reported being on the job greater than 24 months, two for 12 to 24 months, and one for less than 6 months. All, however, reported meeting the required training in the safe use of pesticides as specified in the Florida Statutes, Chapter 482.091(2) (e) (10), which requires 4 hours of classroom training prior to or within six months of employment.

Only one technician reported ensuring that work clothing is kept in a designated laundry basket away from regular soiled clothes. It should be noted, however, that all of this technician's clothes were laundered in the same washing machine. At the same time, product labels of pesticides containing deltamethrin and permethrin, which were widely detected across companies, require that work clothes of applicators not be mixed with regular laundry (Bayer Environmental Science, 2003; Southwest Contract Packaging Company, 2001).

Responses to questions regarding hygienic practices among technicians indicated that only one technician was scrupulous about always changing work clothing and socks daily. Four technicians reported that they did so mostly daily. The data also indicates that, although all technicians reported being trained on the safe use of pesticides, only one reported always using proper footwear and always removing work footwear before going home. Chemical resistant footwear is required when applying these compounds (e.g. Maxxthor EC containing bifenthrin a widely detected pyrethroid across the companies is applied) (Ensystex IV Inc. 2009).

In response to questions designed to determine how much time the technicians spent in pesticide storage areas daily, two technicians reported always having to spend time in such areas on a daily basis, two reported sometimes spending time in storage areas, and one reported scarcely spending time in such areas.

Pyrethroid levels in Air, Dust and Socks

Tables 11-14 below summarize the levels of pyrethroids in air and dust in vehicles and storage areas and in socks of applicators.

Table: 11. Levels of pyrethroids in Company A: Air (ng/m^3), Dust (ng/g) and Socks (ng/pair).

	allethrin	bifenthrin	permethrin	cyfluthrin	cypermethrin	deltamethrin
Company A (Air)						
SV1-FA13	29.5	75.3	103.3	192.9	134.7	BD[b]
SV1-SU14	12.9	32.9	BD	87.3	65.1	BD
SV2-FA13	34.4	90.4	197.1	171.3	196.8	80.8
SV2-SU14	17.8	50.9	98.8	138.0	90.4	41.8
PV1-FA13	29.2	75.1	BD	192.0	139.0	68.7
PV1-SU14	NA[a]	NA	NA	NA	NA	NA
PV2-FA13	47.2	125.1	265.3	160.2	287.2	BD
PV2-SU14	BD	53.9	BD	105.1	95.8	BD
STOR/A-FA13	27.1	68.7	84.8	BD	162.7	BD
STOR/A-SU14	BD	48.3	BD	40.0	39.9	44.3
Company A (Dust)						
SV1-FA13	73.6	1766.7	8267.5	12.7	12596.2	174.9
SV1-SU14	465.2	1517.3	1829.3	3540.3	11272	986.9
SV2-FA13	3.58	115.5	54.6	BD	1166.9	BD
SV2-SU14	2.70	10.1	BD	81.8	583.9	3.32
PV1-FA13	114.8	1030.8	8325.3	12.1	5499.6	279.9
PV1-SU14	NA	NA	NA	NA	NA	NA
PV2-FA13	6.29	165.6	149.1	BD	55.3	BD
PV2-SU14	1942.3	5828.4	1639	43604.5	11755.9	4028.4

Table 11. Continued Levels of pyrethroids in Company A: Air (ng/m^3), Dust (ng/g) and Socks (ng/pair).

	allethrin	bifenthrin	permethrin	cyfluthrin	cypermethrin	Deltamethrin
Company A (Dust)						
STOR/A-FA13	681.2	7172.8	3918.1	54470	161479	1608.8
STOR/A-SU14	783.9	1195.2	112.2	11110.4	9306.5	1683
Tech1-socks-FA13	2997.2	19343.4	109083	BD	811066	774.2
Tech1-socks-SU14	8712.5	28386	29476.6	17102.6	1066737	18024.9
Tech2-socks-FA13	BD	6.64	BD	11.64	139.5	BD
Tech2-socks-SU14	8715.8	27240.4	14082.3	190723	60000	18030.4

[a]NA = not available (no samples were collected), [b]BD = below detection limits, SV = service vehicle, PV = private vehicle, STOR = storage depot

Table 12: Levels of pyrethroids in Company B: Air (ng/g), Dust (ng/g).

	allethrin	bifenthrin	permethrin	cyfluthrin	cypermethrin	deltamethrin
Company B (Air)						
SV1-FA13[c]	30.7	79.2	BD[b]	152.9	139.2	BD
SV1-SU14	NA[a]	NA	NA	NA	NA	NA
STOR/B-FA13	31.5	84.7	BD	155.9	146.6	BD
STOR/B-SU14	NA	NA	NA	NA	NA	NA
Company B (Dust)						
SV1-FA13[c]	61.4	61.4	920.3	1638.2	970.5	136.2
SV1-SU14	NA	NA	NA	NA	NA	NA
STOR/B-FA13	590.1	17407	4454.1	7703.1	92463	1374.5
STOR/B-SU14	NA	NA	NA	NA	NA	NA

[a]NA= not available (no sample taken), [b]BD = below detection limits,[c] = technician used service vehicle as private vehicle to drive home, SV = service vehicle, STOR = storage depot

Table 13 : Levels of pyrethroids in Company C: Air (ng/m^3), Dust (ng/g) and Socks (ng/pair.

	allethrin	**bifenthrin**	**permethrin**	**cyfluthrin**	**cypermethrin**	**deltamethrin**
Company C (Air)						
SV1-FA13[a]	114.0	301.0	691.1	568.1	654.3	BD[b]
SV1-SU14	19.7	72.8	BD	3630.8	BD	46.6
STOR/C-FA13	24.1	61.5	BD	157.8	109.2	BD
STOR/C-SU14	BD	BD	BD	52.1	BD	BD
Company C (Dust)						
SV1-FA13	1918.3	4900.1	426531	67939	208499	4689.8
SV1-SU14	3.49	43.7	133.5	3100.8	6796.5	54.8
STOR/C-FA13	2002	5280.5	14663.9	BD	222992	4673.4
STOR/C-SU14	11792.6	113956	19210	1050249	41229.4	24451.3
Tech1-socks-FA13	10759.1	78256.8	621715	3211.7	4717789	36121.2
Tech1-socks-SU14	BD	73.5	340.2	969.7	2532.6	BD

[a]technician used service vehicle as personal vehicle to drive home, [b]BD = below detection limits, SV = service vehicle, STOR = storage depot

Table 14; Levels of pyrethroids in Company D: Air (ng/m^3), Dust (ng/g) and Socks (ng/pair).

	allethrin	bifenthrin	permethrin	cyfluthrin	cypermethrin	deltamethrin
Company D (Air)						
SV1-FA13[a]	38.9	111.0	107.1	BD	308.0	BD[b]
SV1-SU14	70.6	197.4	BD	495.3	343.3	BD
Company D (Dust)						
SV1-FA13	141.1	7324.7	897.4	879.4	671.3	341.6
SV1-SU14	15.5	BD	24.3	446.3	264.6	18.4
Tech1-socks-FA13	6.8	1077.9	122.1	29.7	630.3	15.7
Tech1-socks-SU14	788.2	247.7	4528.8	14956	200435	16.4

[a]Technician used service vehicle as personal vehicle to drive home, [b]BD = below detection limits, SV = service vehicle

Levels of Pyrethroids in Air in Service Vehicles. Two service vehicles were made available for sampling for Company A while for the other three companies only one service vehicle was available. Samples were collected during two periods, Fall 2013 and Summer 2014, in service vehicles for Companies A, C and D. The service vehicle for Company B was no longer available for sampling during the second sampling period. Figure 5 shows an overall comparison of all pyrethroid detection in service vehicles. Figures 6 – 9 show the results when comparing air levels inside service vehicles between the two sampling periods for each company.

Overall, air levels inside service vehicles for individual pyrethroids ranged from below detection to 3,631 ng/m^3. Levels were generally higher in samples collected from Service Vehicle #1 from Company C collected during Fall 2013 and the highest

individual level (3,631 ng/m^3) was for cyfluthrin in the same vehicle but during the Summer 2014 sampling campaign. These levels indicate that applicators could be chronically exposed to measurable quantities of pyrethroids.

Levels of all six pyrethroids were higher during Fall 2013 when compared to Summer 2014 for both service vehicles for Company A. For the service vehicle for Company C, levels were higher during Fall 2013 for four of the six pesticides (allethrin, bifenthrin, permethrin and cypermethrin) but lower for cyfluthrin and deltamethrin. For Company D, levels were higher during Summer 2014 for four of six pesticides (allethrin, bifenthrin, cyfluthrin and cypermethrin) and lower only for permethrin.

Company C was the largest of the four companies and could likely be handling more pyrethroids and therefore contributing to higher levels. Furthermore, a soiled bee suit and sprayer were present in the driver compartment of the service vehicle sampled. On the other hand, one would expect that company C, being the larger company, would exercise more oversight to reduce vehicle contamination and to protect technician's safety. Since we did not set out to determine whether this was the case, we cannot make that assumption.

Although Florida does not experience markedly different Summer and Fall seasons as is the case in more northern locations, temperatures are generally higher during Summer. Thus, one would expect more pyrethroids in the air during the Summer due to higher temperatures causing volatilization. However, the temperature in the cab of the trucks are influenced by the use of air conditioning and whether or not windows are closed which could affect these values, making it more difficult to make conclusive statements regarding the influence of temperature on the levels measured.

Another factor which could influence the levels in air is simply the quantities used during both seasons. Generally it would be expected that greater levels of pyrethroids are applied during Summer, which would contribute to higher levels during this sampling period.

The higher levels of of pyrethroids in the air of company D's service vehicle during the Summer 2014 sampling period could be due to the difference in pyrethroid use in this company when compared with the others.

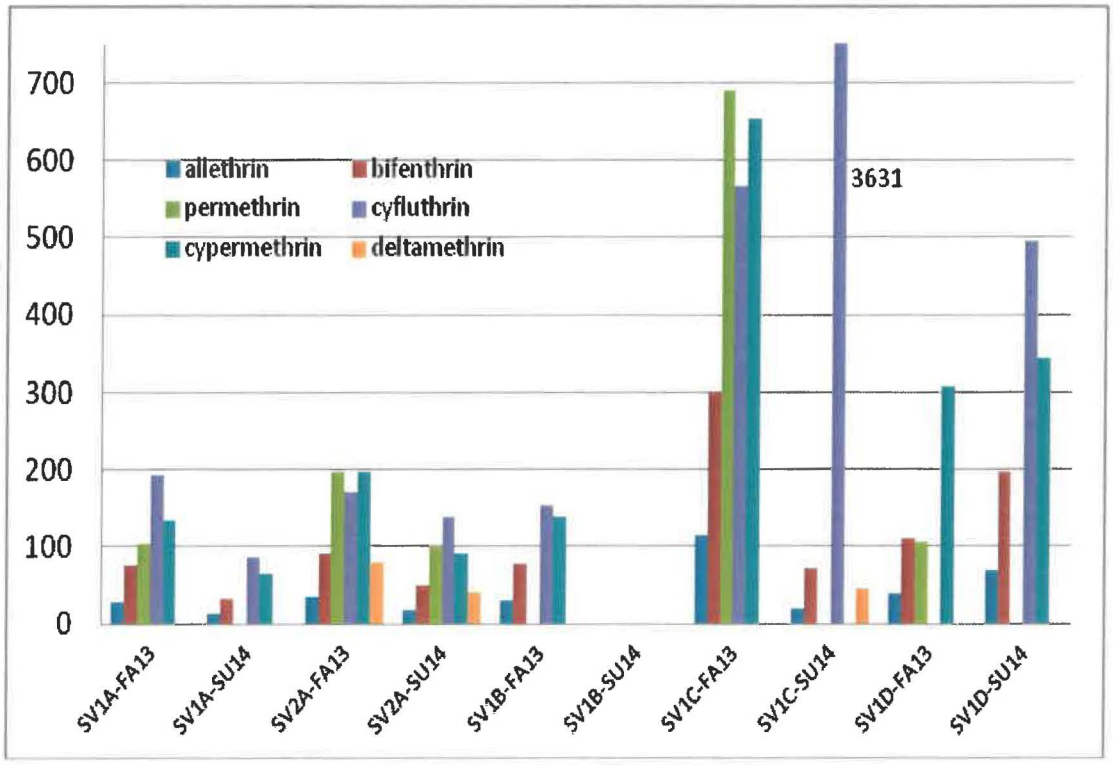


Figure 6: Levels of pyrethroids in the air of service vehicles in ng/m^3.

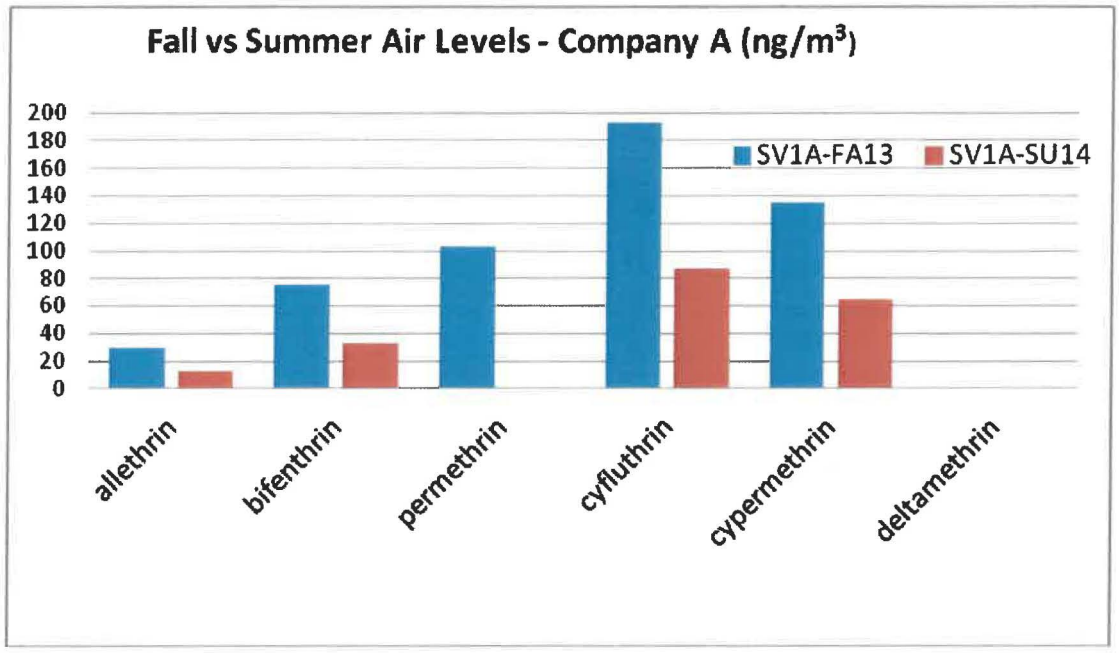


Figure 7: Levels of pyrethroids in air of service vehicle 1 - Company A (ng/m^3).

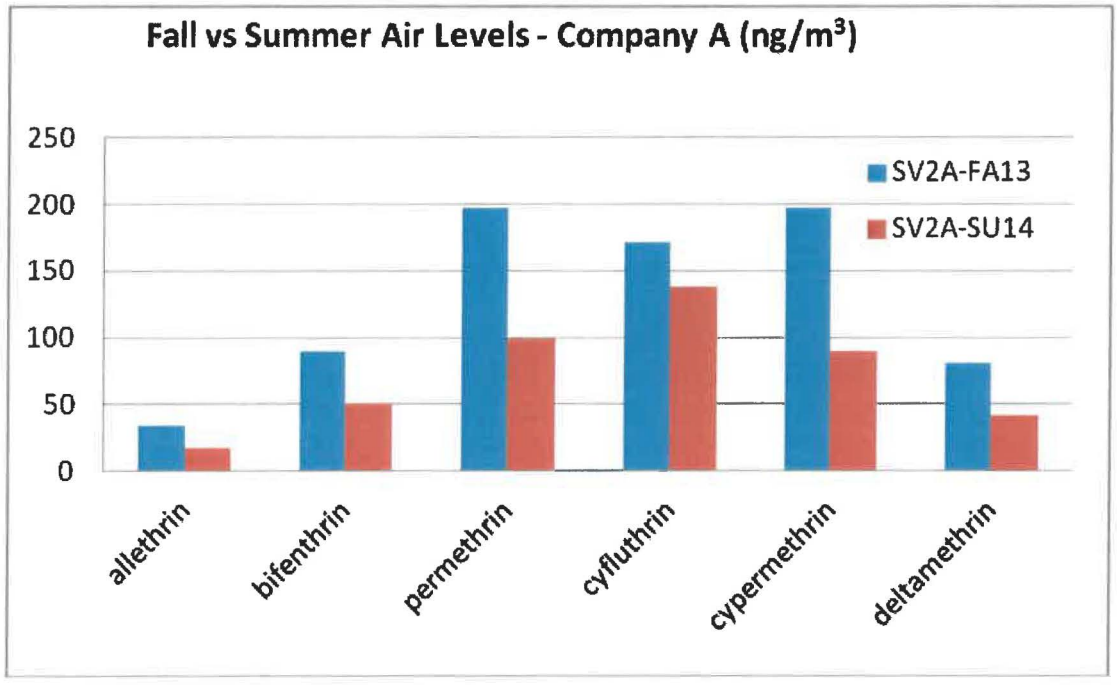


Figure 8: Levels of pyrethroids in air of service vehicle 2-Company A.

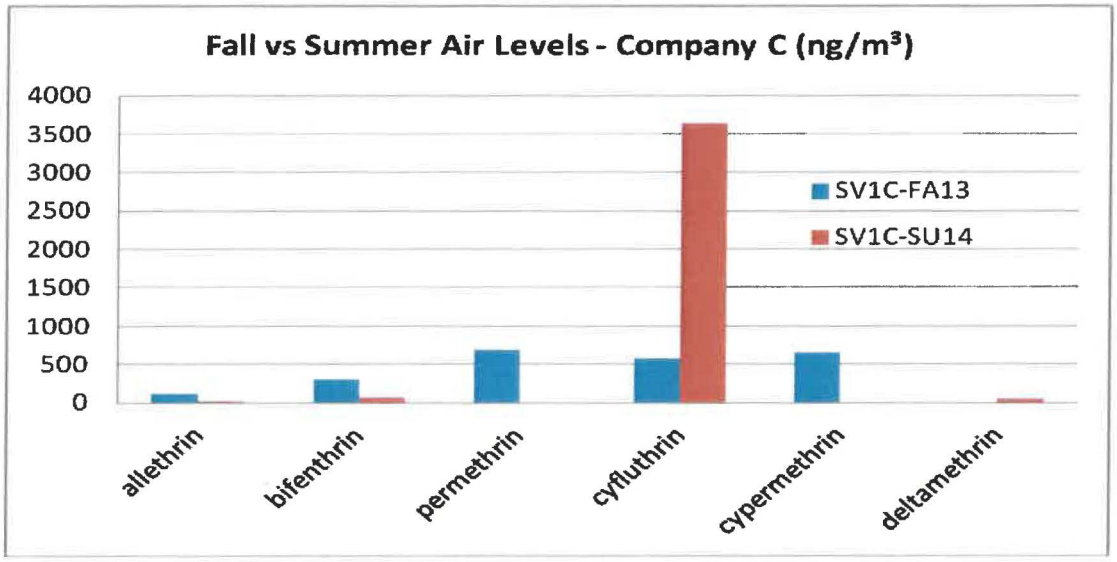


Figure 9: Levels of pyrethroids in air of service vehicle-Company C.

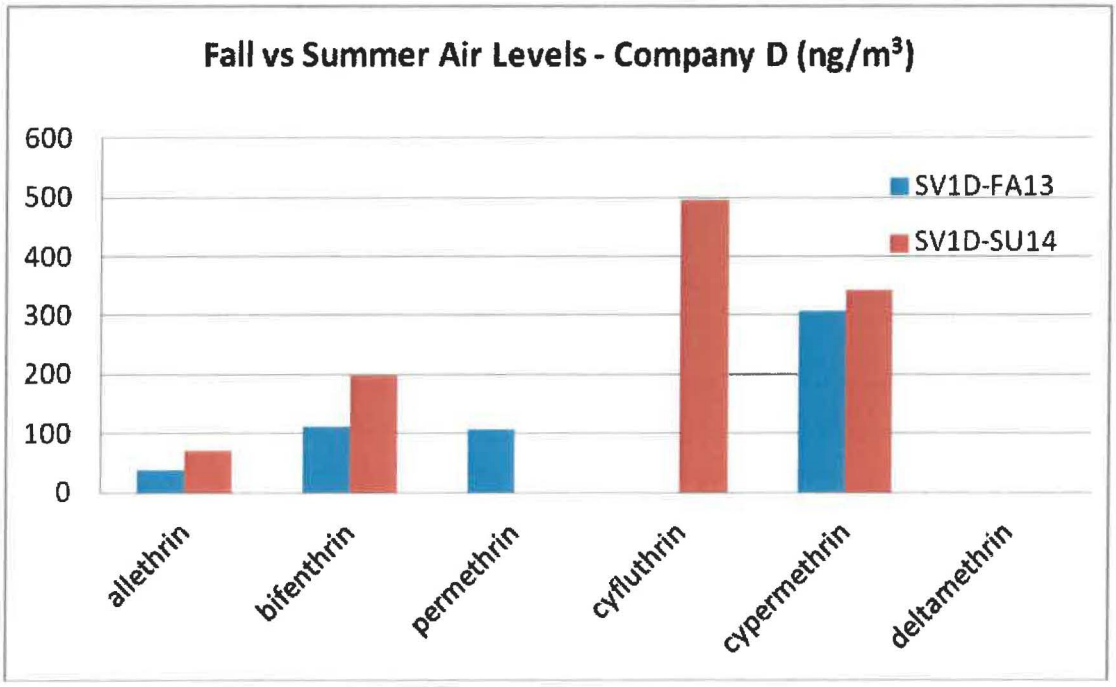


Figure 10: Levels of pyrethroids in the air of service vehicle—Company D.

Levels of Pyrethroids in Air in Private Vehicles. Only in the case of Company A did technicians drive service vehicles that were different than their private vehicles. In addition, only in the case of private vehicle #2 for Company A were we able to collect air samples during both sampling periods.

Overall, levels of individual pyrethroids in air in the two private vehicles of Company A ranged from below detection to 287 ng/m^3 in private vehicle #2, as shown in Figure 11 below. A comparison of levels in private vehicles #1 and #2 during the same sampling period (Fall 2013) shows that levels were higher for 4 pyrethroids (allethrin, bifenthrin, permethrin, and cypermethrin) in private vehicle #1 and higher for 2 (cyfluthrin and deltamethrin) in private vehicle #2 (Figure 12). Reasons for these differences are unclear at this time but may reflect differences in the behavior of the applicators who drive these vehicles.

A comparison of levels between Fall 2013 and Summer 2014 in private vehicle #2, shows that levels were higher during the Fall 2013 sampling campaign than during Summer 2014 for all pyrethroids except deltamethrin (Figure 11). This agrees exactly with the results of service vehicle #1 for Company A.

The levels of four of six pyrethroids (allethrin, bifenthrin, permethrin, and cypermethrin) were higher in the second private vehicle for company A than the levels of the same pyrethroids in the air of storage and service vehicles of company A. This suggests that the technician could be using his private vehicle to transport pesticides or might have been moonlighting and practicing pest control out of his private vehicle.

Total pyrethroids levels were similar in personal vehicles compared with service vehicles, ranging from 255 ng/m^3 to 885 ng/m^3 (Figure 13). This suggests that technicians are transferring chemicals from their work environment to their personal vehicles, increasing the likelihood of take-home exposure.

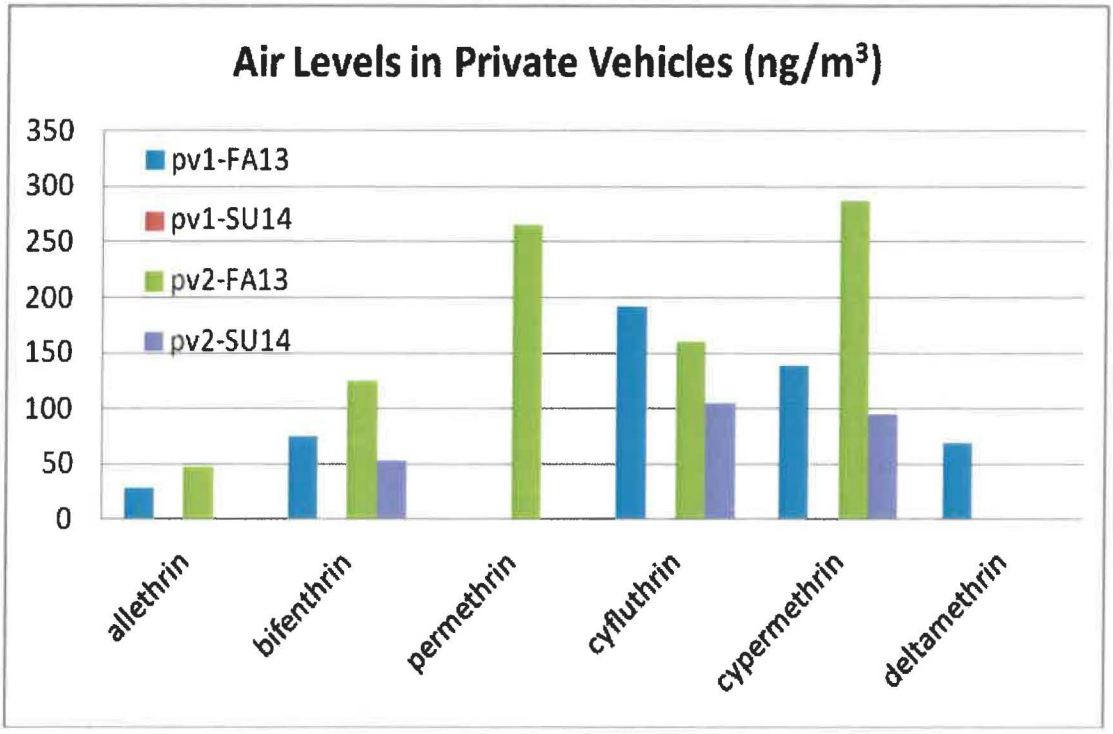


Figure 11: Levels of pyrethroids in the air in private vehicles: Company A.

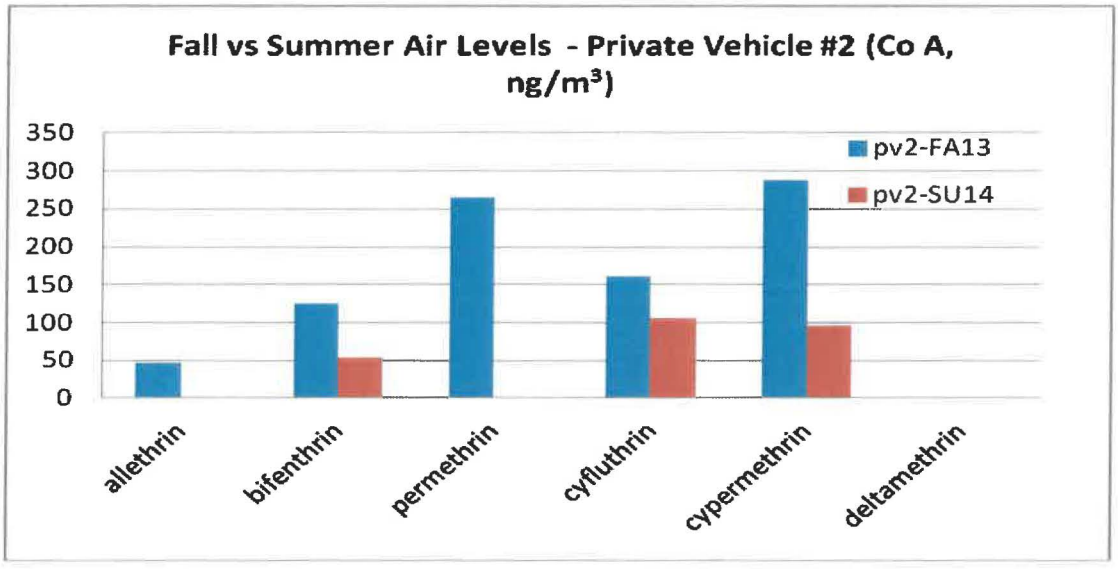


Figure 12: Fall vs. Summer air levels of pyrethroids in private vehicle#2 (Company A).

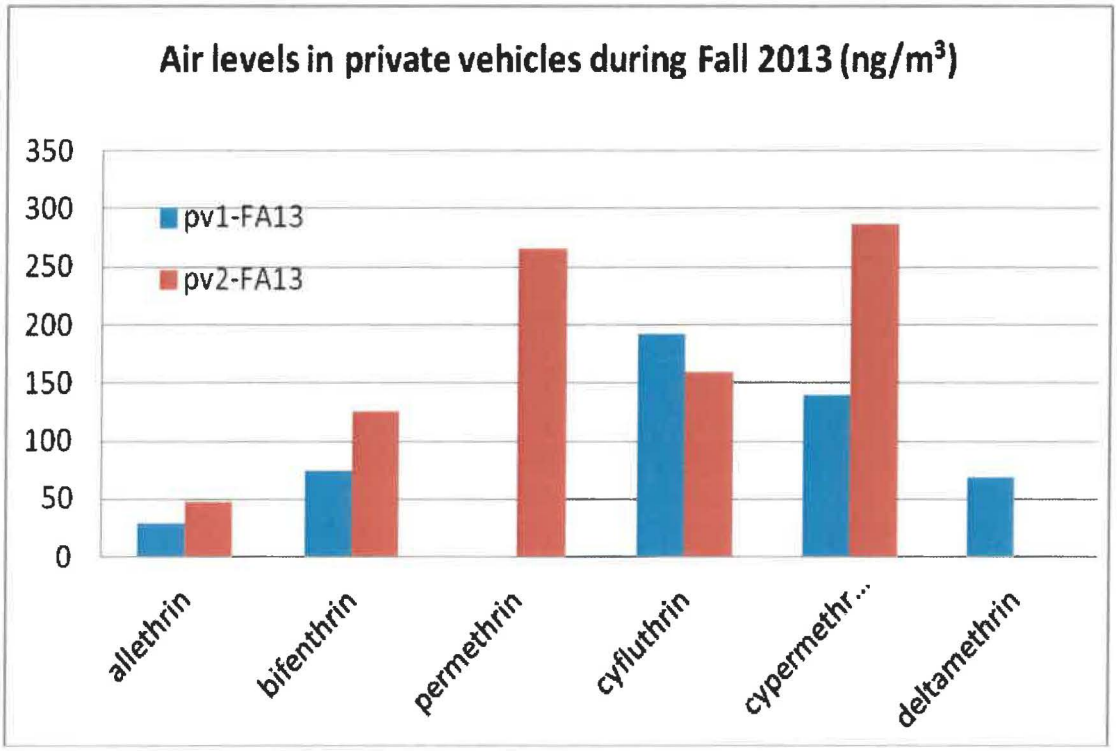


Figure 13: Comparison of levels of pyrethroids in air of private vehicles during Fall 2013.

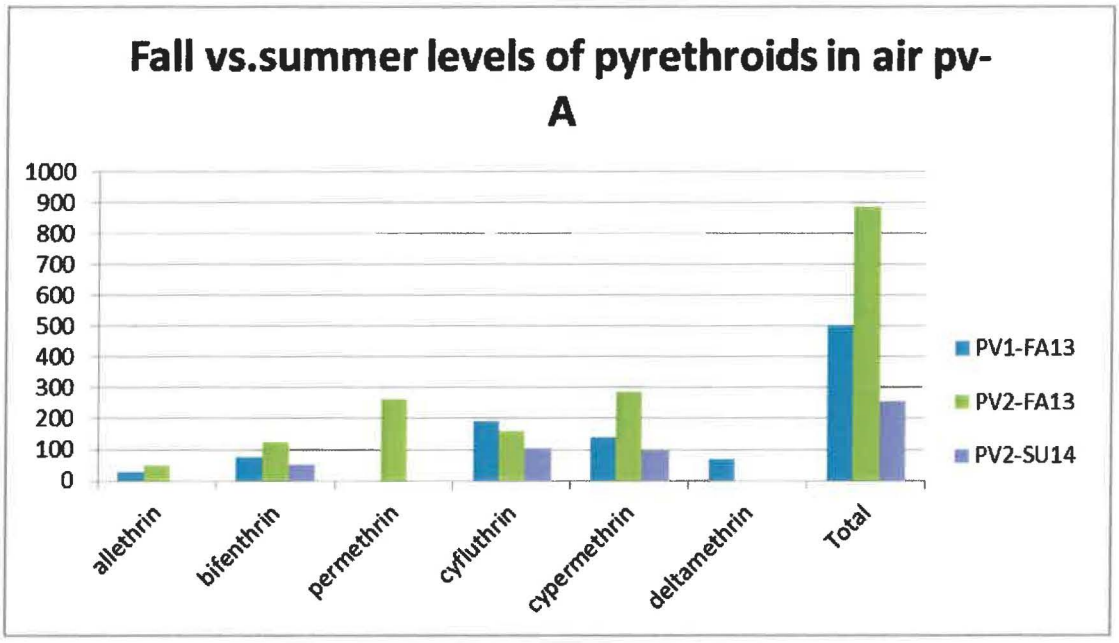


Figure 14: Total levels of pyrethroids in the air of private vehicles.

Levels of Pyrethroids in Air in Storage Depots. Only companies A, B and C had storage depots. However, company B was not available for sampling during Summer 2014. The highest individual level was in the air of the storage depot for Company A when compared with the storage depots for Companies B and C (Figure 15). In the storage depot of Company A, levels ranged from below detection to 163 ng/m^{3}during Fall 2013 and from below detection to 48 ng/m^3 during Summer 2014 (Figure 16.a) Levels in the storage depot of Company B ranged from below detection to 156 ng/m^3 (Figure 15) and in the storage depot of Company C from below detection to 158 ng/m^3 (Figure 16.b).

In Company A levels in Fall 2013 were higher for allethrin, bifenthrin, permethrin and cypermethrin, while levels in Summer 2014 were higher for cyfluthrin and deltamethrin (Figure 16.a). Similarly, Figure 16.b shows that levels were higher for Company C during Fall 2013 for four pyrethroids (allethrin, bifenthrin, cyfluthrin and

cypermethrin) while levels of permethrin and deltamethrin were below detection limits during both periods.

The size, contents and ventilation of storage areas, as well as spillage are just some of the factors that could affect the levels of pyrethroids detected. The storage depot of Company C is comprised of an independent shed while that of Company B was a room of the office building and Company A's was inside of a garage. Pyrethroids are semi volatile organic compounds and the differences in temperatures in the different storage areas could also affect the levels in air.

The total pyrethroids found in air in storage depots ranged from insignificant to 419 ng/m^3. This suggests that the possibility of technicians being exposed to pyrethroids in this environment varies.

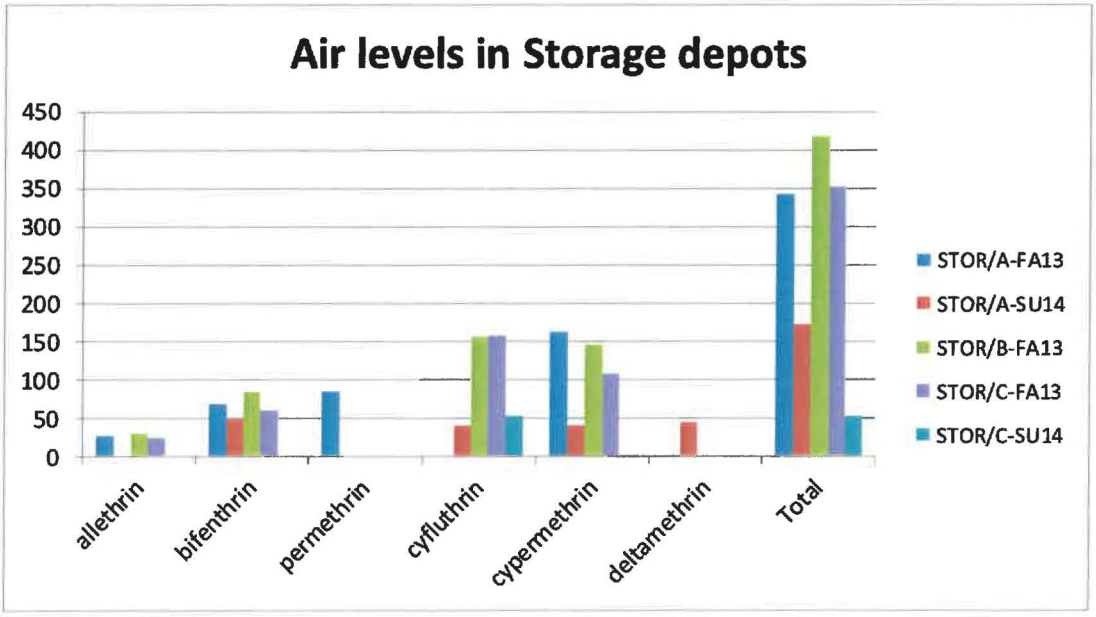


Figure 15: Levels of pyrethroids in air of storage depots.

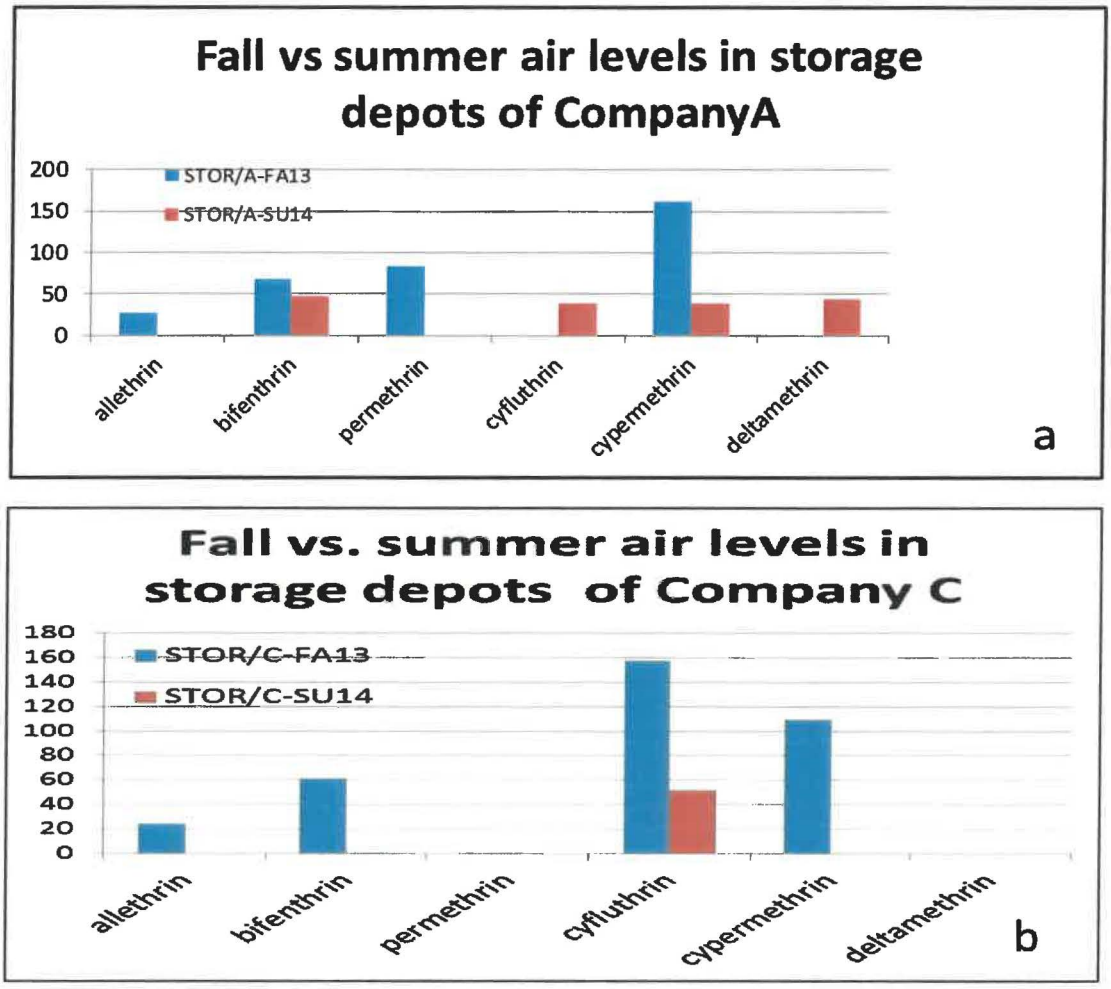


Figure16: Fall vs. Summer pyrethroid levels in air of storage depot of Company A and Company C

Levels of Pyrethroids in Dust in Service Vehicles. Figure 17 shows the levels of pyrethroids measured in dust from service vehicles. Levels were highest by a large margin in the service vehicle for Company C during Fall 2013 for 5 of 6 pyrethroids, and second highest for the sixth. With regards to total pyrethroids, levels were much higher (714,477 ng/g) in this vehicle compared to all others. Service vehicle #1 from Company A showed high levels during both sampling periods (22,892 ng/g during Fall 2013 and 19,611 ng/g during Summer 2014), followed by the service vehicle for Company D

during Fall 2013 (10,256 ng/g) and service vehicle for Company C during Summer 2014 (10,133 ng/g). All other vehicles showed much lower levels of pyrethroids in dust.

Figures 18 - 21 shows that in all cases levels were higher during Fall 2013 compared to Summer 2014. The highest levels of individual pyrethroids in the dust from company C service vehicle in Fall 2013 (Figure 17), compared with other service vehicles is consistent with the highest levels detected in the air of the same service vehicle and period (Figure 5). Also, the higher detections in total pyrethroid levels in dust during the Fall 2013 levels than the Summer 2014 levels is similarly consistent with the levels in air for the same period. This shows that the airborne and dust-bound concentrations may be positively related as pyrethroids adsorbed to particles and surfaces may become airborne (Elflein et al., 2003; Butte and Heinzow, 2002) due to thermal desorption and re-adsorption.

Total pyrethroids in service vehicle dust ranged from 402 ng/g to 714,477 ng/g. These values are significant and indicate that pyrethroids are being released in service vehicles and can therefore result in chronic exposure for applicators.

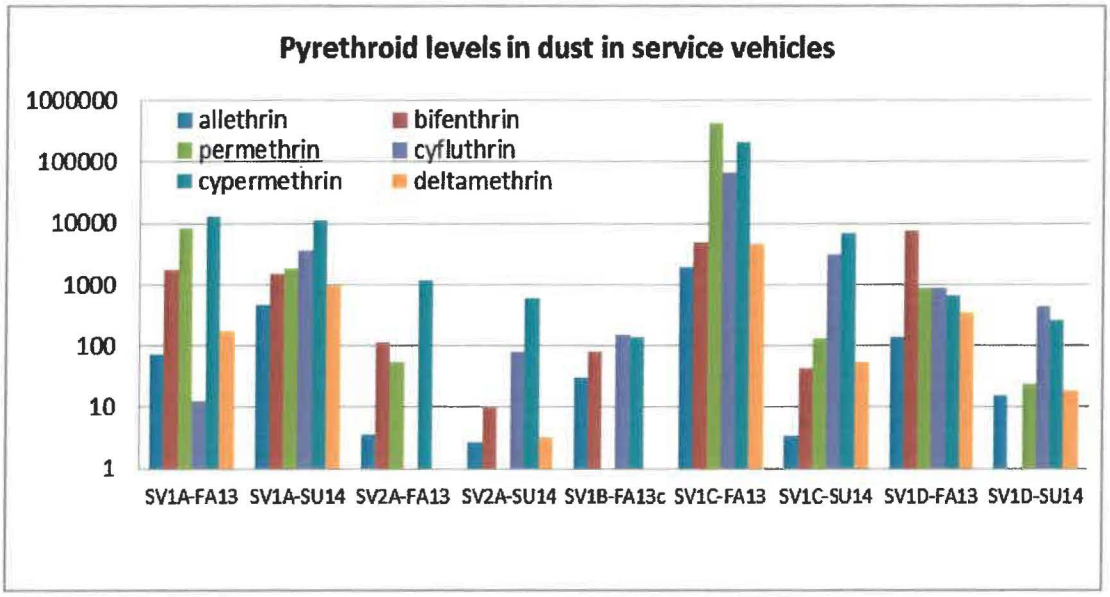


Figure 17: Pyrethroid levels in dust in service vehicles of pest control companies.

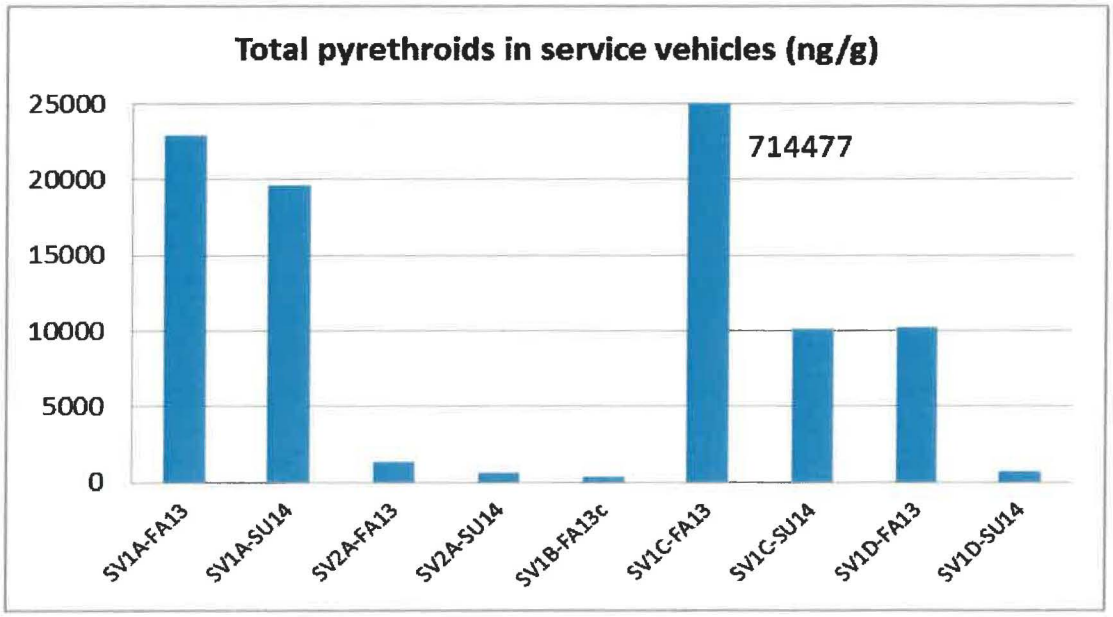


Figure: 18. Total pyrethroids in service vehicle dust (ng/g).

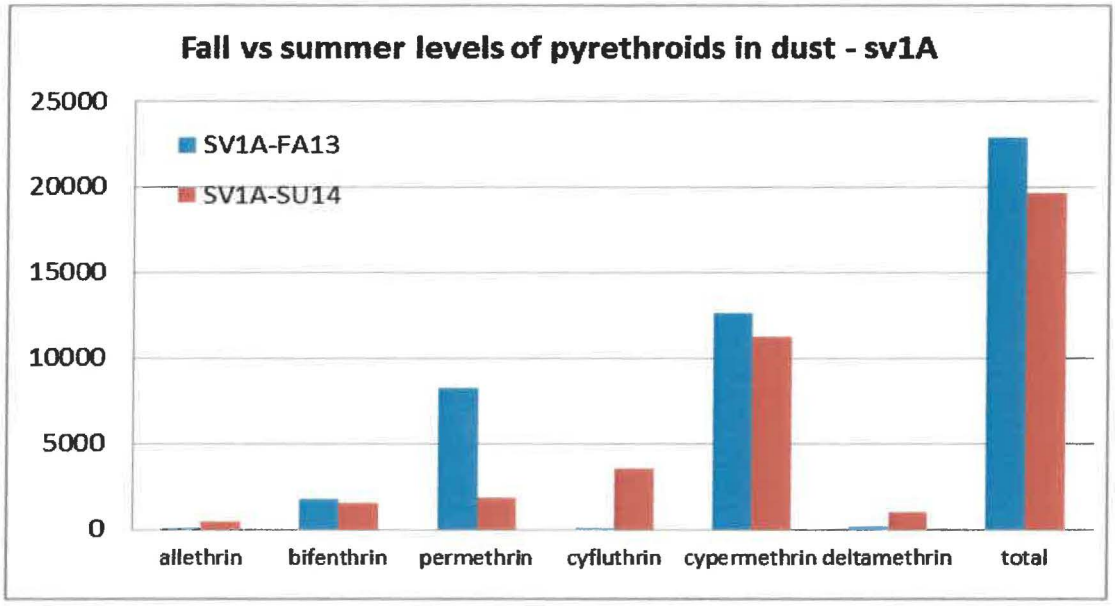


Figure: 19. Comparison of levels of pyrethroids during fall vs. summer periods—SV 1A.

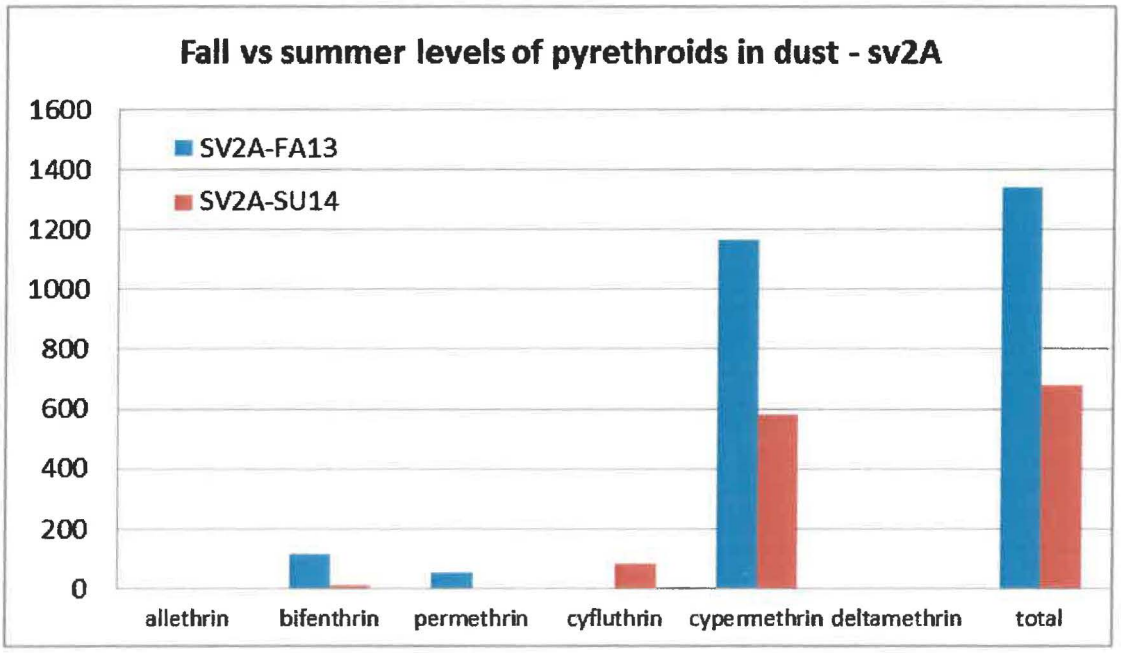


Figure 20: Comparison of levels of pyrethroids during fall vs. summer periods SV2A.

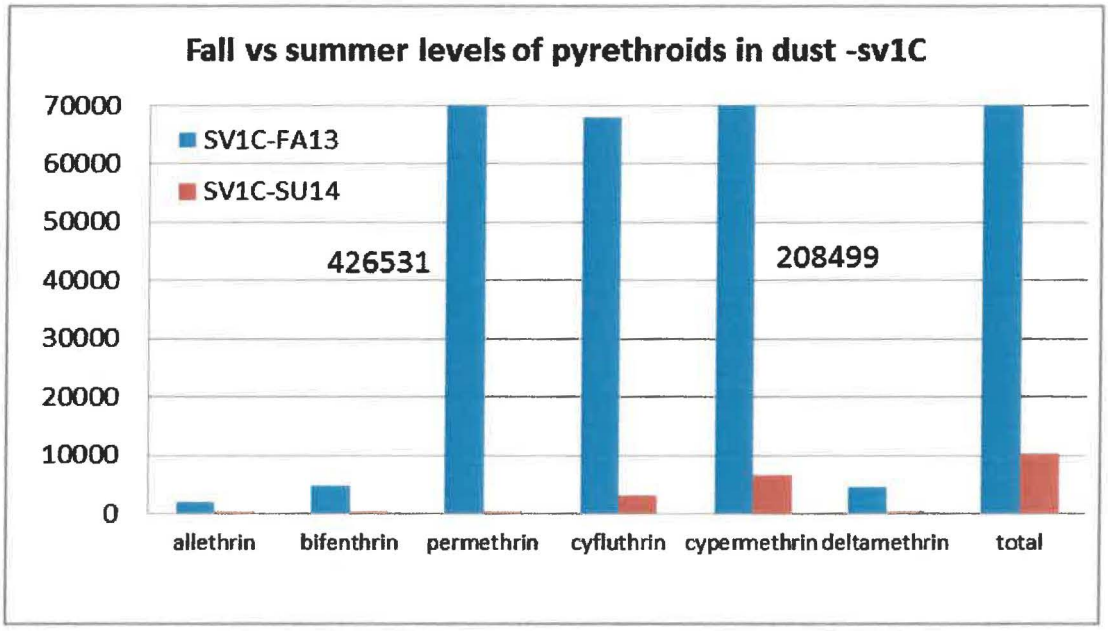


Figure: 21. Comparison of levels of pyrethroids during fall vs. summer periods— SV1C.

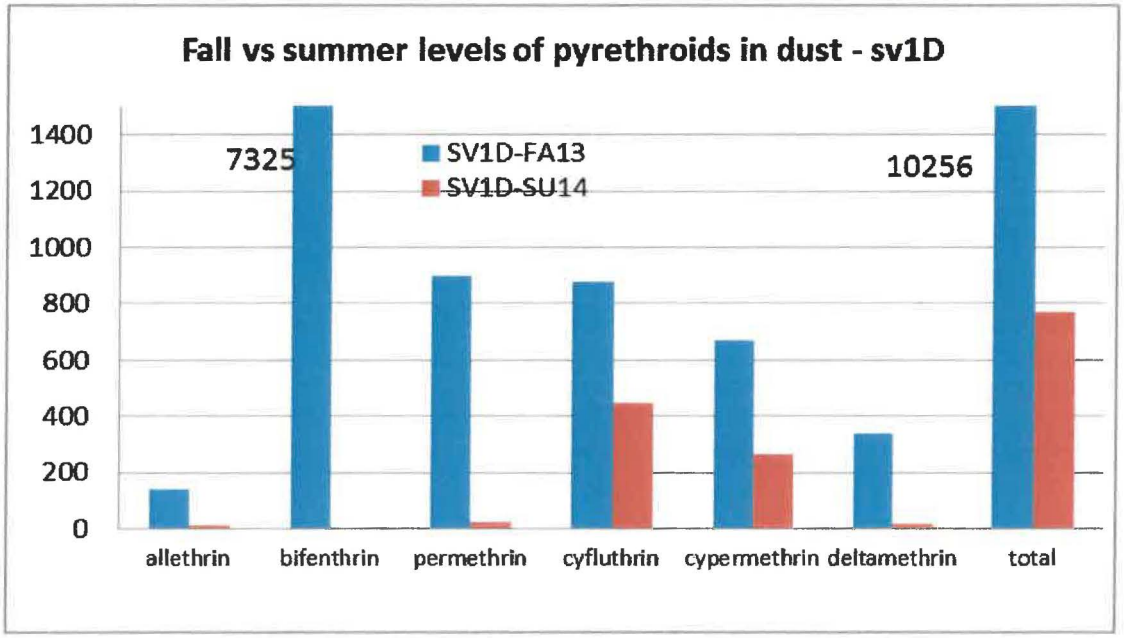


Figure: 22. Comparison of levels of pyrethroids during fall vs. summer periods—SV1D.

Levels of Pyrethroids in Dust in Personal Vehicles. Only in the case of Company A did technicians drive service vehicles that were different than their private vehicles and only in the case of private vehicle #2 were we able to collect dust samples during both sampling periods.

Overall, levels of individual pyrethroids ranged from below detection to 43,605 ng/g for cyfluthrin in private vehicle #2 during Summer 2014. In fact, levels were highest for all individual pyrethroids in this vehicle during this period except for permethrin (highest in private vehicle #1). These results are shown in Figure 22 below.

In terms of total pyrethroids, values ranged from private vehicle #2 Summer 2014 (68,799 ng/g) > private vehicle #1, Fall 2013 (15,263 ng/g) > private vehicle #2, Fall 2013 (377 ng/g).

A comparison of Fall versus Summer levels in private vehicle #2 indicates that levels were much higher during Summer 2014 than Fall 2013 (Figure 22 below). This is the opposite of the trend for pyrethroids in air in this private vehicle. This may be due to pyrethroids adsorbing strongly to dust and volatilizing to air more readily during the warmer Summer sampling period when compared with the cooler Fall period. These values, however, indicate that personal vehicles not used in work activities are being contaminated, most likely via contaminated work gear (clothing, shoes, etc.).

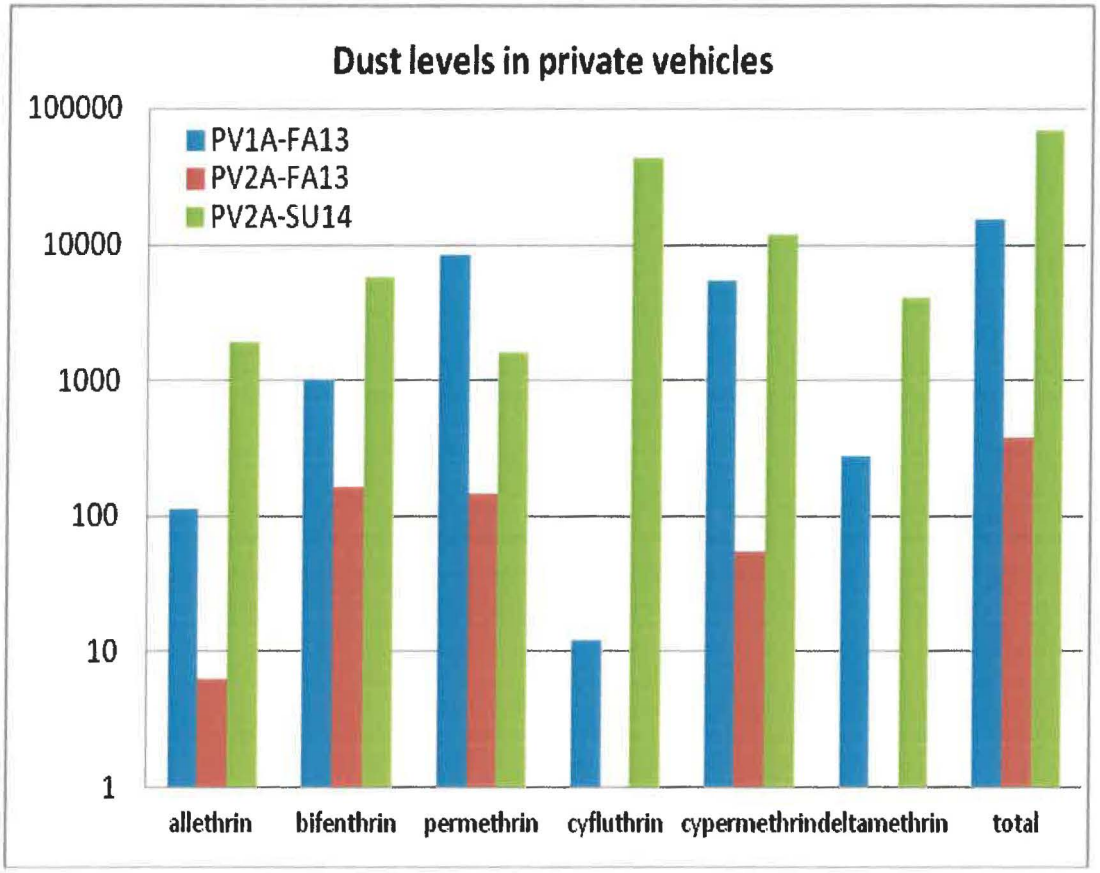


Figure 23: Comparison of levels of pyrethroids in dust in private vehicles.

Levels of Pyrethroids in Dust in Storage Depots. Samples were obtained from storage depots in Companies A, B and C. Fall and Summer samples were obtained from storage depots in Companies A and C but only in Fall for the storage depot in Company B.

Overall, levels of individual pyrethroids ranged from below detection to 1,050,249 ng/g for cyfluthrin in the storage depot of Company C during Summer 2014, (Figure 24). Levels were in fact highest for all pyrethroids except cypermethrin for this

storage depot during this sampling period (cypermethrin levels were highest in this storage depot but during Fall 2013).

Regarding total pyrethroids, levels were in the order of Company C storage depot, Summer 2014 (1,260,888 ng/g) > Company C storage depot, Fall 2013 (249,612 ng/g) > Company A storage depot, Fall 2013 (229,330 ng/g) > Company B storage depot, Fall 2013 (123,992 ng/g) > Company A storage depot, Summer 2014 (24,191 ng/g).

A comparison of Fall versus Summer levels indicates dissimilar results for Companies A and C. In the case of the storage depot of Company A, levels were higher for 4 pyrethroids (bifenthrin, permethrin, cyfluthrin, and cypermethrin) and only slightly lower for two pyrethroids during the Fall 2013 sampling period. In the case of the storage depot of Company A, however, levels of 5 pyrethroids were higher during the Summer 2014 sampling period and lower only for cypermethrin. It is unclear why this would be the case. The results may be due to differences in the types of pesticides used (i.e. different active ingredients).

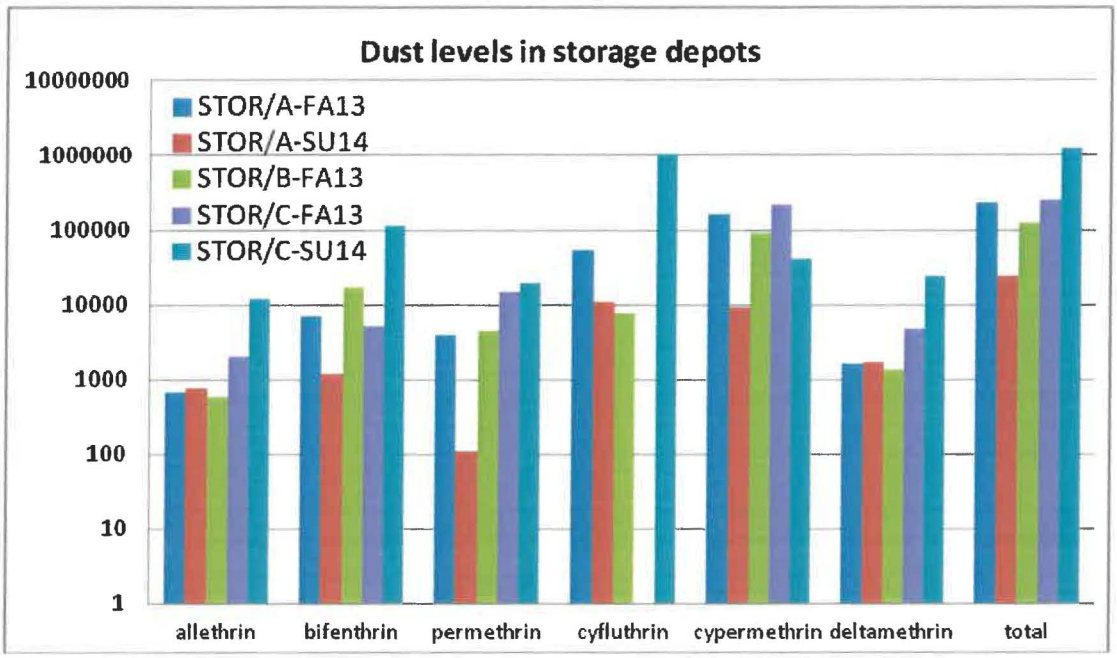


Figure 24: Levels of pyrethroids in dust in storage depots in ng/g.

While technicians' hygiene practices, spillages and differences in management practices at the companies could affect levels in dust, the fact that pyrethroids bind readily to soil (Schlier, 2011) could contribute to the levels detected in dust. Overall, these high levels indicate that there is a good chance that workers are being exposed to significant levels via inhalation of dust.

Levels of Pyrethroids in Technicians' Socks. We were able to obtain socks from two technicians from Company A, and one technician each from Companies C and D. In all cases we were able to obtain samples during Fall 2013 and Summer 2014.

Levels of individual pyrethroids ranged from below detection to 4,717,789 ng of cypermethrin in the socks of the technician from Company C during Fall 2013 (Table 14). Levels were in fact highest for all pyrethroids except cyfluthrin in this sample.

In terms of total pyrethroids, levels were in the order of Company C technician, Fall 2013 (5,467,853 ng) > Company A technician #1, Summer 2014 (1,168,440 ng) > Company A technician #1, Fall 2013 (943,264 ng) > Company A technician #2, Summer 2014 (318,792 ng) > Company D technician, summer 2014 (220,972 ng) > Company C technician, Summer 2014 (3,916 ng) > Company D technician, Fall 2013 (1883 ng) > Company A technician #2, Fall 2013 (158 ng).

A comparison of pyrethroid levels in socks collected during Fall 2013 versus Summer 2014 indicates that levels were consistently higher during the Summer period for the socks from Company A's technicians #1 and #2 and Company D's technician. Interestingly, the opposite was the case for the socks collected from the technician from Company C, in which levels were higher in all cases during the Fall of 2013 than in the Summer of 2014 (Figure 25).

Employee hygiene and safety practices could contribute to the level of pyrethroids detected in socks. Company C's technician, who reported never using chemical resistant footwear when required, had the highest total level of pyrethroids in his socks during Fall 2013. The levels in socks were generally high in all companies and even Company D's technician, who reported always wearing chemical resistant footwear, also had high levels of pyrethroids in his socks. These levels support the hypothesis that pest control technicians are transporting pyrethroids home in their socks and exposing themselves and their families to these chemicals.

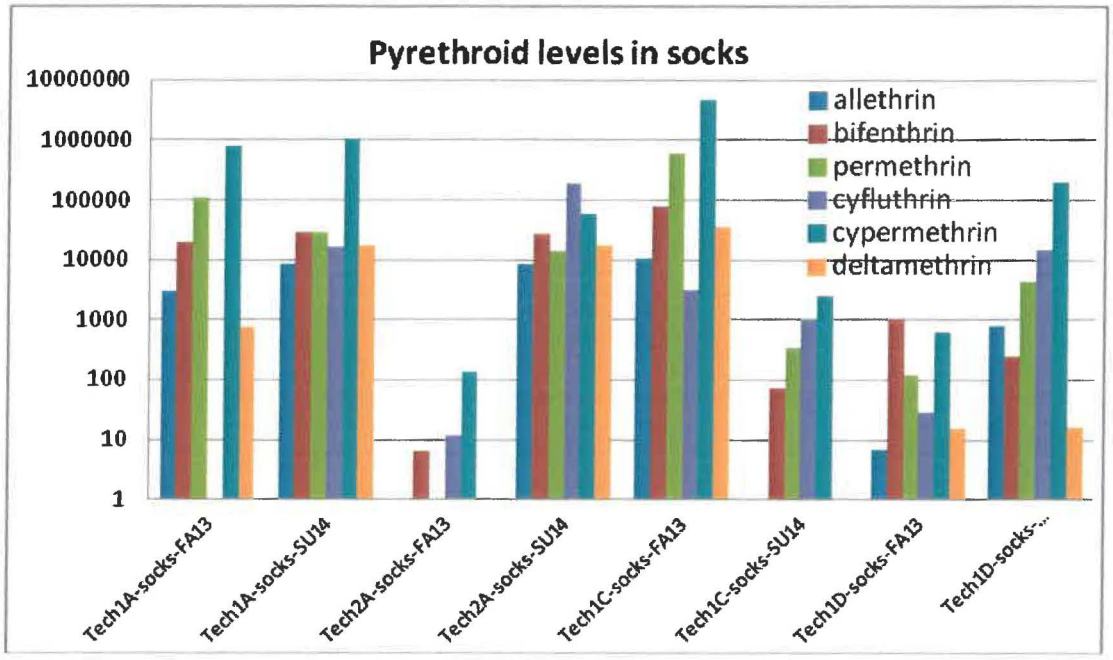


Figure 25: Pyrethroid levels in socks in ng/pair.

Exposure to Pyrethroids in Dust

Scientists agree that inhalation of contaminated dust represents the most likely exposure route for humans to organic pollutants. Therefore, we decided to calculate exposure to pyrethroids on the basis of total levels of pyrethroids in dust measured in the study. In calculating estimated exposure to pyrethroids we used the USEPA average dust ingestion rates of 4.16mg/day for adults and an average adult body weight of 70 kg.We also assumed a 100% ingestion rate of dust, as per USEPA suggestion.

The estimated exposure was calculated using the formula:

Exposure (ng/day/kg) = (C x IR) / body weight (1)

Where,

C = concentration (ng/g), IR = ingestion rate (mg/day) (2)

The exposure in dust was calculated for each sampling event in company storage, service vehicle and personal vehicle. Table 15 shows the results.

The comparisons are presented in Figure 25. Overall, exposure was much higher at the storage depot of Company C (74.9 ng/kg/day during Summer 2014 and 14.8 ng/kg/day for Fall 2013), the service vehicle from Company C during Fall 2013 (42.5 ng/kg/day) and the storage depot of Company A during Fall 2013 (13.6 ng/kg/day).

There is no data for inhalation minimum risk levels (MRLs) for pyrethroids. However, intermediate term oral MRL of 0 .2mg/kg/day based on a no-adverse-effect-level (NOAEL) of 15.5mg/kg/day for neurotoxicity has been recommended for permethrin (USDHHS, 2003), one of the commonly detected pyrethroids in this study. Values higher than this were calculated for the service vehicle in Company C during Summer 2014 and the storage depot for this company during Fall 2013, although this was based on total pyrethroids. Company C was the largest, which may help explain the highest exposure rates there.

Table 15: Total pyrethroid exposure across sampling site/matrix.

Total pyrethroid exposure in each sample matrix	
Sampled Matrix	Total pyrethroid exposure (ng/kg/day)
A/SV1-FA13	1.360
A/SV1-SU14	1.165
A/SV2-FA13	0.080
A/SV2-SU14	0.041
A/PV1-FA13	0.907
A/PV2-FA13	0.022
A/PV2-SU14	4.089
STOR/A-FA13	13.629
A/PV2-SU14	1.438
B/SV1-FA13[c]	0.225
B/STOR/B-FA13	7.369
C/SV1-FA13	42.460
C/SV1-SU14	0.602
STOR/C-FA13	14.834
STOR/C-SU14	74.933
D/SV1-FA13	0.609
D/SV1-SU14	0.046

The exposure rates that were calculated in this study also fall within the ranges that have been calculated for other groups of pesticides, flame retardants and polychlorinated biphenyls, suggesting that chronic exposure to pyrethroids should be a cause for concern.

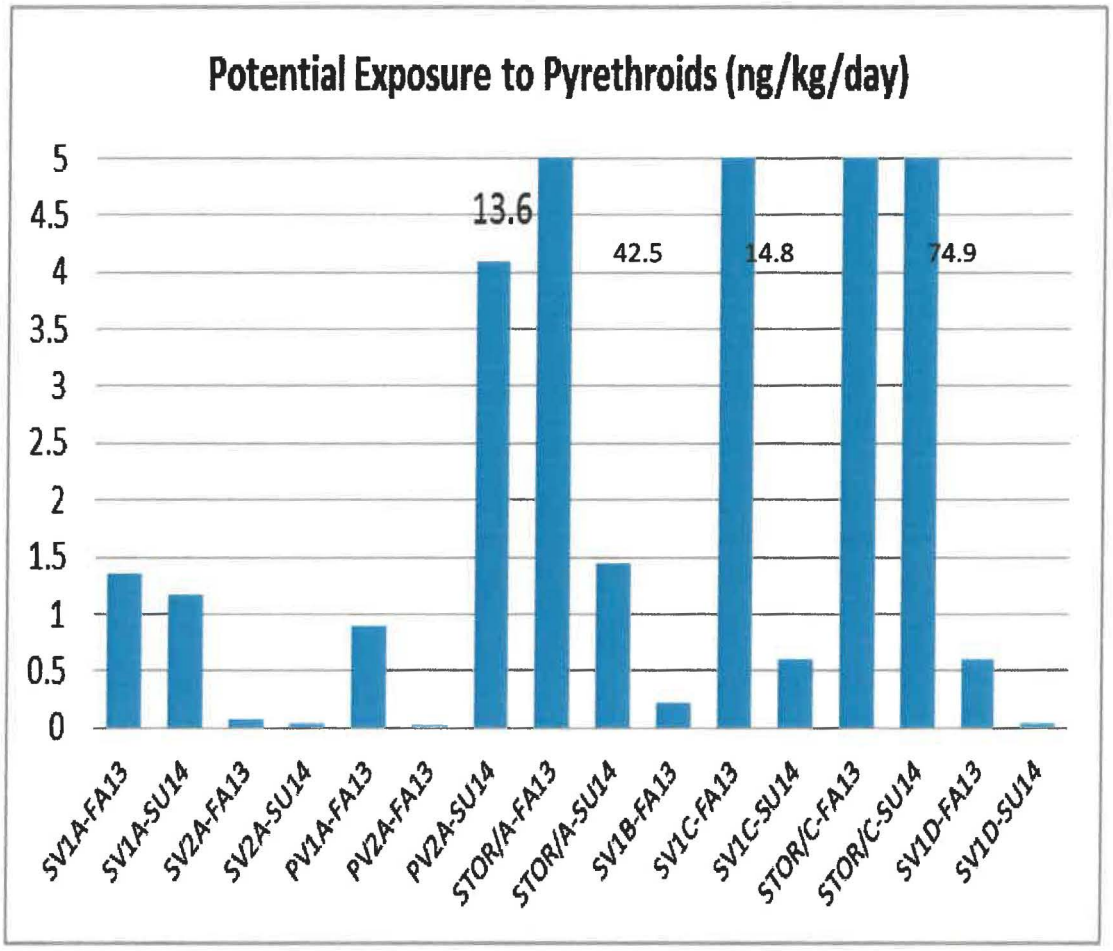


Figure 26. Exposure to pyrethroids across locations and time.

Levels of Pyrethroids vs. Training, Experience Safety and Hygiene Practices.

Since technician experience, training and hygiene practices could influence the concentrations of pyrethroid in the sample matrices of interests, we present the relationship between these factors and concentrations of pyrethroids in Figures 27-29. Figure 27 shows that in service vehicles levels were consistently lower during both sampling periods for the technician with over 24 months experience in Company A,

(A/SV2-FA13/>24 & A/SV2-SU14/>24). The trend does not hold across companies as in the case of the technician who operates the service vehicle for Company B (B/SV1-FA13/>24), the levels were much higher. For private vehicles, in Company A, levels in the private vehicle of the technician with 0-6 months experience (PV1 (0-6 months) were higher than levels in the private vehicle of the technician with more than 24 months' experience (PV2 (>24 months). This suggests that company practices, as well as personal hygiene practices and experience, influence levels and therefore exposure.

Figure 27 shows clearly that, for each sampling period (which may influence total levels), pyrethroid levels were consistently higher in the socks of technicians who never wear protective footware nor change their footwear before going home. This supports the idea that hygiene practices are related to exposure levels.

Furthermore, since annual recertification of pesticide applicators requires safety training, technicians with more time on the job would, in theory, be more careful to adhere to these practices which could reflect in lower levels of pyrethroid in vehicles that they used. Training in the proper use of PPE has been shown to reduce loads of pesticide residues (Van Der Jagt et al., 2004).

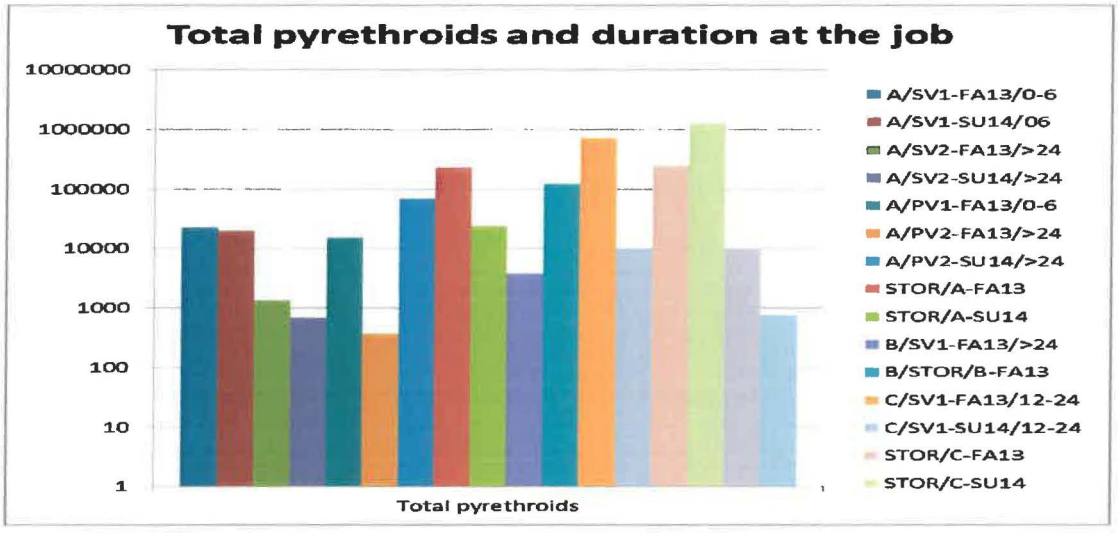


Figure 27: Total pyrethroids and duration on the job.

*All technicians have received the minimum training in the safe use of pesticides.

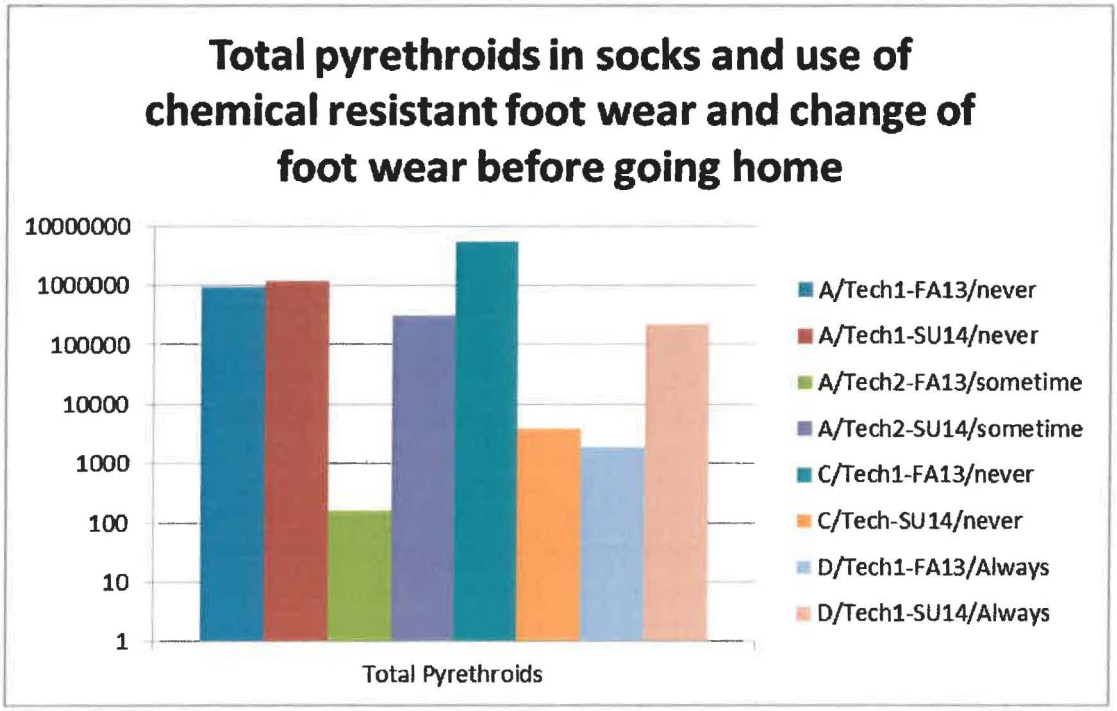


Figure: 28. Total pyrethroids in socks and use of chemical resistant foot wear and change of foot wear.

Potential Take-home Exposure and Technicians' Time on the Job

Since the potential take-home exposure is given by the concentration of pyrethroids present in the socks and personal vehicles of pest control technicians, we present the concentration of pyrethroids in personal vehicles and technicians' time on the job in Table 16. The concentrations in socks and technicians' training and time on the job are presented in Table 17 and Figures 29 and 30.

Table: 16 Pyrethroid levels (ng/g) in dust of personal vehicles and technicians' time on the job.

Pyrethroid levels (ng/g) in dust of personal vehicles and technicians time on the job*			
	PV1-FA13/0-6 month	PV2-FA13/>24 month	PV2-SU14/>24 month
Total Pyrethroids	9762.9	376.29	68798.5

* All technicians received the minimum training in the safe use of pesticides

Table 17: Pyrethroid levels (ng/pair of socks) and technician's time on the job.

Pyrethroid levels (ng/g) in socks of technicians and time on the job and training*				
	Tech1-socks-FA13/0-6	Tech2-socks-FA13/> 24	Tech1-socks-SU14/0-6	Tech2-socks-SU14/> 24
Total Pyrethroids	943263.8	157.78	1168439.6	318791.9

* All technicians received the minimum training in the safe use of pesticides

Figure 29 shows that for the same sampling period levels were much lower in the personal vehicle of the technician with > 24 months experience compared with the levels in the personal vehicle of the technician with only 0 – 6 months experience. This shows that more experienced technicians use better practices which result in lower levels of pyrethroids in their vehicles.

Figure 30 shows that during both sampling periods pyrethroid levels in socks are lower for technicians with more experience on the job. This supports the theory that the greater the experience of technicians, the more careful they are to adhere to good hygienic practices.

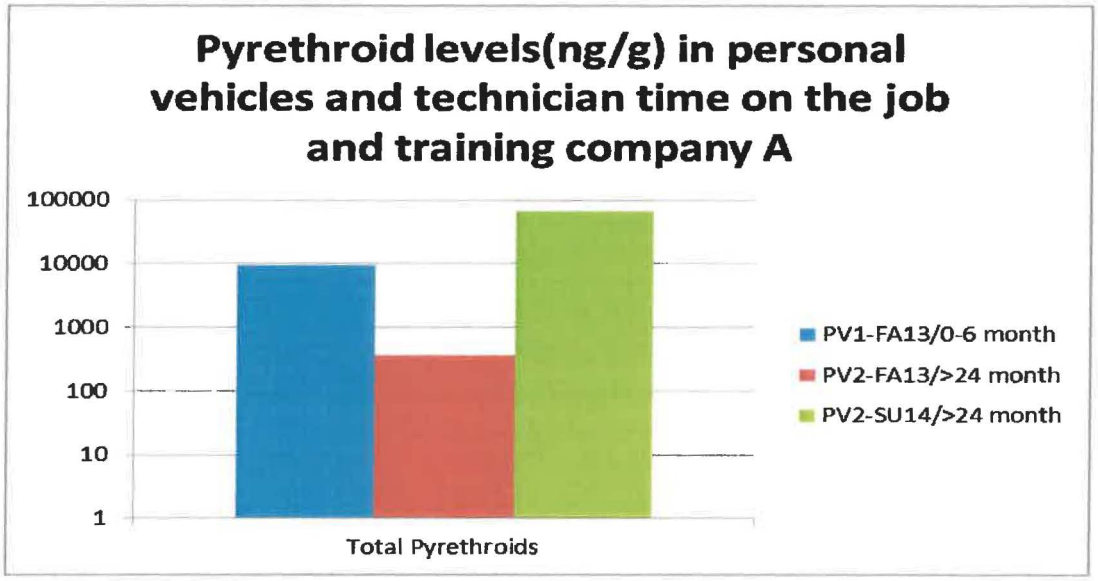


Figure 29: Pyrethroid levels in personal vehicles and technicians time on the job and training

Note: All technicians received the minimum required training

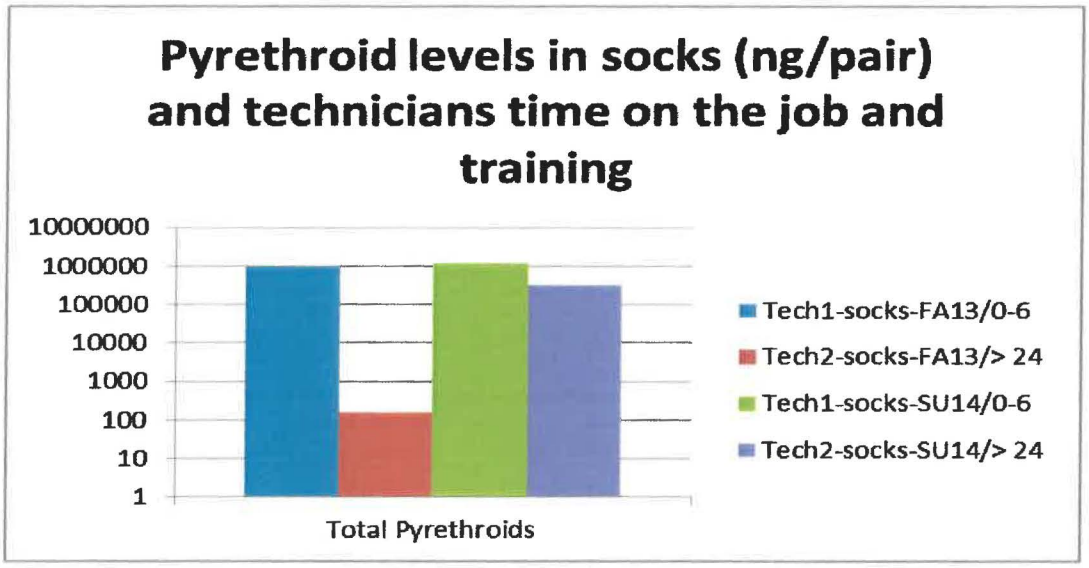


Figure 30. Pyrethroids in socks and technicians time on the job.

Conclusion

Levels of pyrethroids in air and dust of service vehicles, private vehicles and storage depots of pest application companies were varied but high enough in many cases to be a cause of concern for the health of application technicians. Results suggest that technicians may be transferring pyrethroids from storage areas and application sites to service vehicles and personal vehicles and perhaps from service vehicles to private vehicles. Exposure calculations indicate that at least in some environments applicators are subjected to exposure rates elevated high enough to be of concern. The consistent measurement of pyrethroids in air and dust of private vehicles and on socks of applicators suggests a strong potential for take-home exposure.

On the positive side, these results suggest that greater care in the training and monitoring of technicians' hygienic practices can prevent or minimize exposure.

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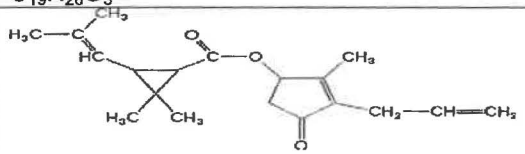
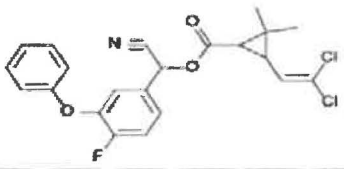
APPENDICES

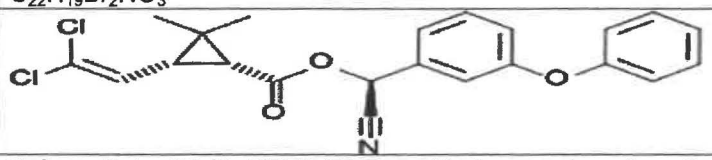
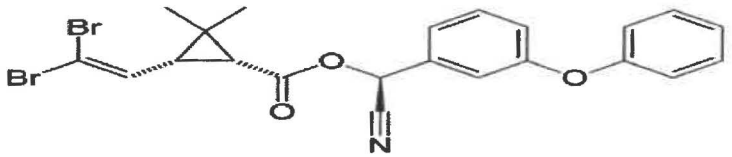
Appendix A

Table A1: Chemical identities of selected pyrethroids, modified from (USDHS, 2013)

Characteristics	Name and Detail [a]
Name	Allethrin - 2-methyl-4-oxo-3-(2-propenyl)-2-cyclopenten-1-yl 2,2-dymethyl -3-(2-methyl-1-propenyl) cyclopranecarboxylate
Ratio of isomers	≥ 95% (1R)-isomers; ≥ 75% trans-isomers
CAS registry	584-79-2
Chemical Formula	$C_{19}H_{26}O_3$
Chemical Structure[b]	
Name	Cyfluthrin-Cyano (4-fluoro-3-phenoxyphenyl)methyl 3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate
Ratio of isomers	Unstated stereochemistry
CAS registry	68359-37-5
Chemical Formula	$C_{22}H_{18}C_{l2}FNO_3$
Chemical Structure[b]	

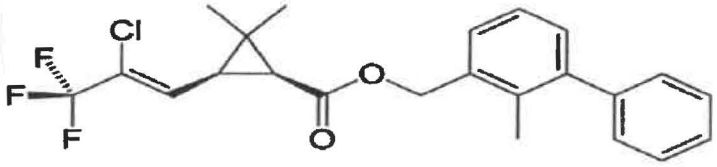
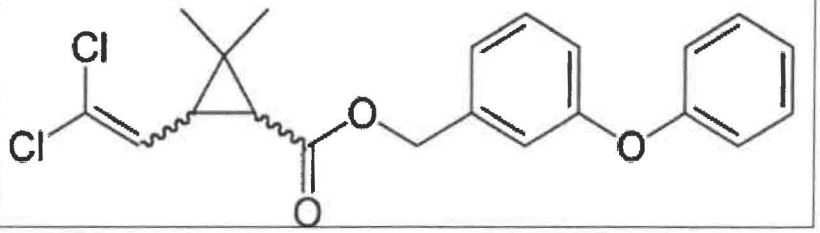
Appendix A (Continued)

Table A1: Continued Chemical identities of selected pyrethroids, from (USDHS, 2013)

Characteristics	Name and Detail [a]
Name	Cypermethrin- Cyano(3- phenoxyphenyl)methyl 3-(2,2-dichloroethenyl)-2,2- dimethylcyclopropanecarboxylate
Ratio of isomers	Unstated stereochemistry
CAS registry	52315-07-8
Chemical Formula	$C_{22}H_{19}Br_2NO_3$
Chemical Structure [b]	
Name	Deltamethrin -[IR-[1a(S*),3a]]-Cyano (3-phenoxyphenyl) methyl 3-(2,2- dibromo ethenyl)-2,2-dimethylcyclopropanecarboxylate,decamethrin
Ratio of isomers	≥ 98% single
CAS registry	52918-63-5
Chemical Formula	$C_{22}H_{19}Br_2NO_3$
Chemical Structure [b]	
Name	trans-Cypermethrin D6
Ratio of Isomers	mixture of c(R(cyano)1R3S/S(cyano)1S3R) and D(R(cyano)1S3R/S(cyano)1R3S
CAS Registry	82523-65-7
Chemical Formula	$C_{22}D_6H_{13}C_{l2}NO_3$
Chemical Structure [c]	

Appendix A (Continued)

Table A1 continued Chemical Identities of selected modified from (USDHHS, 2013)

Characteristic	Name and Detail [a]
Name	Bifenthrin -(2-methyl[l,1'-biphenyl]-3-yl) methyl 3-(2 - chloro-3,3,3-trifluoro-1-propenyl) -2,2– dimethylcyclopropane- carboxylate
Ratio of Isomers	≥97% cis- isomer
CAS Registry	82657-04-3
Chemical Formula	$C_{23}H_{22}ClF_3O_2$
Chemical Structure[b]	
Name	Permethrin (3-Phenoxyphenyl) methyl3-2,2 dichlorophenyl)-2,2-dimethylcyclopropane-carboxylate
Ratio of Isomers	(1R,trans):(1R,cis):(1S, trans):(1S,Cis =3:2:3:2
CAS Registry	52645-53-1
Chemical Formula	$C_{21}H_{20}Cl_2O_3$
Chemical Structure [b]	

Note: [a] is taken from (USDHHS, 2003) and [b] Chemical Structures from (Feo, Eljarrat, Barceló 2010) while CAS means Chemical Abstract Service. [c] Chemical structure is from Dr. Ehrenstorfer Standards samples http://www.lgstandards.com/epages

Appendix B

Table B1: Basic questions relating to technicians training, work and hygiene

Employment				
1. How long have you worked with this company?				
0-6 months	7-12months	13-24 months	> 24 month	
2. Have you received training in handling pesticide safely?				
A. Yes	B. No			
Hygiene and Personal Protective Equipment				
0 Never	1 Scarcely	2 Sometimes	3.Most times	4 Always
4.On a scale of 0 to 4 where 0 means never and 4 means always, how often Do you change out of the boots that you work in and wear different shoes home?				
0 Never	1 Scarcely	2 Sometimes	3 Most times	4 Always
5.On a scale of 0 to 3 where 0 means never daily and 2 means always daily, How often do you change your work socks?				
0 Never daily	1 Mostly daily	2 Always daily		
6. On a scale of 0 to 2 where 0 means never daily and 2 means always daily. How often do you change your shirt/ pants?				
0 Never daily	1 Mostly daily	2 Always daily		
7. Where at home do you store your soiled work cloths until they are laundered?				
A. Designated laundry basket	B. With the regular laundry			
Job Related				
8. On a scale of 0 to 4 where 0 means never and 4 means always, how frequent Does your job require that you go to the pesticide storage area?				
0.Never	1.Scarcely	2.Sometimes	3.most times	4.Always
9. What insecticide was applied out of your service vehicle today?				
10. What insecticide is in your chemical inventory?				

Appendix B (Continued)

Table B2: Data used to determine breakthrough and percentage recovery

Data used to Determine Break Through Percentage Recovery	
Flow Rate	*Volume of air in m^3*
3 liter/minute	0.8357, 0.7352, 0.8324
5 liter/minute	0.8267, 0.6735, 0.7942
Dust	
weight of dust	1g
volume of D6 cypermethrin	100 µ L
Concentration of D6 cypermethrin	10ppm
PUF plug	
1 Plug	1 plug
volume of D6 cypermethrin	100 µL
Concentration of D6 cypermethrin	10ppm
Socks	1 pair
volume of D6 cypermethrin	100 µL
Concentration of D6 cypermethrin	10ppm

Table B3: List of pyrethroids which were in the inventory of company B

Pyrethroid inventory at Company B		
Fall Sampling Period		
Product	**Formulation**	**Active Ingredients**
Cy Kick CS	Liquid	Cyfluthrin 6%
SWCP Permethrin Granules	Granular	Permethrin 0.25%
CB 80	Aerosol	Pyrethrins 0.05%
Maxxthor EC	Emulsifiable Concentrate	Bifenthrin ,23.4% by Wt Cis 97 % min, trans 3% max
Maxxthor SC	Suspension concentrate	Bifenthrin 7.9% by wt, Cis 97% min Trans 3% Maximum
Demon Max	Emulsifiable Concentrate	Cypermethrin 25.3 % Cis/trans ratio Min 45%± Cis and max 55% ± trans
Cyper TC	Liquid	Cypermethrin 25.4% Cis/trans ratio 47/53 ± 10%
Tempo SC Ultra	Suspension concentrate	β Cyfluthrin 11.8%

Appendix B (Continued)

Table B4: List of pyrethroid products which were in inventory at company D

Pyrethroid inventory at Company D		
Fall Sampling Period		
Product	**Formulation**	**Active Ingredients**
Bifen XTS Insecticide/Termiticide	Liquid	Bifenthrin 25.1 % by wt, Cis 97 % min Trans 3 % Maximum
Cyper TC	Liquid	Cypermethrin 25.4% Cis/trans ratio 47/53 ± 10%
Summer sampling		
Bifen XTS Insecticide/Termiticide	Liquid	Bifenthrin 25.1 % by wt, Cis 97 % min Trans 3 % Maximum

Notes Products in inventory includes products in tool boxes in the bed of work trucks
Products in storage

Appendix B (Continued)

Table B5: List of pyrethroid products that were in the inventory of company A

Pyrethroid inventory at Company A		
Fall Sampling Period		
Product	**Formulation**	**Active Ingredients**
Talstar ® Professional Insecticide	Liquid	Bifenthrin 7.9 % by wt, Cis 97 % min Trans 3 % Maximum
Cyper TC	Liquid	Cypermethrin 25.4% Cis/trans ratio 47/53 ± 10%
Suspend SC	Suspension concentrate	Deltamethrin 4.75 % .42ibs per gallon
Demon Max	Emulsifiable Concentrate	Cypermethrin 25.3 % Cis/trans ratio Min 45%± Cis and max 55% ± trans
Cy-kick CS	Liquid	Cyfluthrin 6%
MasterLine Insecticide	Liquid	Bifenthrin 7.9 % by wt, Cis 97 % min Trans 3 % Maximum
Suspend SC	Suspension concentrate	Deltamethrin 4.75 % .42ibs per gallon
Bifen XTS Insecticide/Termiticide	Liquid	Bifenthrin 25.1 % by wt, Cis 97 % min Trans 3 % Maximum
Delta Dust insecticide	Dust	Deltamethrin 4.75 % .42 l bs per gallon
Summer Sampling Period		
Talstar ® Professional Insecticide	Liquid	Bifenthrin 7.9 % by wt, Cis 97 % min Trans 3 % Maximum
Cyper TC	Liquid	Cypermethrin 25.4% Cis/trans ratio 47/53 ± 10%
Suspend SC	Suspension concentrate	Deltamethrin 4.75 % .42ibs per gallon
Demon Max	Emulsifiable Concentrate	Cypermethrin 25.3 % Cis/trans ratio Min 45%± Cis and max 55% ± trans
Cy-kick CS	Liquid	Cyfluthrin 6%
MasterLine Insecticide	Liquid	Bifenthrin 7.9 % by wt, Cis 97 % min Trans 3 % Maximum
Delta Dust R insecticide	Dust	Deltamethrin 4.75 % .42 l bs per gal

Appendix B (Continued)

Table B6: List of pyrethroids that were in inventory at Company C

Pyrethroid inventory at Company C		
Fall sampling Period		
Product	**Formulation**	**Active Ingredients**
Cyper TC	Liquid	Cypermethrin 25.4% Cis/trans ratio 47/53 ± 10%
Talstar ® Professional Insecticide	Liquid	Bifenthrin 7.9% by wt, Cis 97% min Trans 3% Maximum
Conquer Residual Insecticide	Liquid	Esfenvalerate Residual Insecticide concentrate 3.48%
Demon Max	Emulsifiable Concentrate	Cypermethrin 25.3 % Cis/trans ratio Min 45%± Cis and max 55% ± trans
Demon WP	Wettable Powder	Cypermethrin 40% ,cis/trans ratio 45/55± 10 %
Delta dust(R) Insecticide	Dust	Deltamethrin 0.05%
Suspend SC	Suspension concentrate	Deltamethrin 4.75 % .42ibs per gallon
Cy-kick Cs	Liquid	Cyfluthrin 6%
Summer Sampling Period		
Cyper TC	Liquid	Cypermethrin 25.4% Cis/trans ratio 47/53 ± 10%
Talstar ® Professional Insecticide	Liquid	Bifenthrin 7.9% by wt, Cis 97% min Trans 3% Maximum
Conquer Residual Insecticide	Liquid	Esfenvalerate Residual Insecticide concentrate 3.48%
Demon Max	Emulsifiable Concentrate	Cypermethrin 25.3 % Cis/trans ratio Min 45%± Cis and max 55% ± trans
Demon WP	Wettable Powder	Cypermethrin 40% ,cis/trans ratio 45/55± 10 %
Delta dust(R) Insecticide	Dust	Deltamethrin 0.05%
Suspend SC	Suspension concentrate	Deltamethrin 4.75 % .42 lbs per gallon
Cy-kick Cs	Liquid	Cyfluthrin 6%
Tempo SC Ultra Insecticide	Suspension concentrate	β Cyfluthrin 11.8%
Dragnet SFR Termiticide Insecticide	Liquid	Permethrin

Appendix B (Continued)

Table B7: Special observations and items per sampling locations and company.

	Company A		Company B	Company C	Company D
Items/Locations sampled	A1 Observations by Items/location	A2 Observations by Items/location	Observations by Items/location	Observations by Items/location	Observations by Items/location
Vehicles					
Service Vehicle type	Pick Up	Pick up _ Cab plus	Pick up	Pickup	Pickup Cab plus
Service Vehicle Floor	vinyl	Vinyl	Vinyl	Vinyl	Carpet
Service Vehicle Contents	Pesticide Container Sprayer F	EI	EI	Bee Suit F Sprayer F	EI EI
Personal Vehicle Type	Pick Up	Sedan	NA	NA	NA
Personal Vehicle Floor	Vinyl	Carpet	NA	NA	NA
Storage					
Storage location	Home Garage	Home Garage	Cabinet in office	Independent	NA
Storage Floor	Concrete	Concrete	Vinyl	wooden	NA
	Inventoried pesticides, Empty Containers, EI Opened containers	Inventoried items ,empty containers	EI	NA	NA NA
Socks					
	Black F White S	Blue F White S	NA NA	Blue F White S	Blue F White S