UNIVERSITY OF ALBERTA

DECONTAMINATION BY LAUNDERING OF TEXTILES SOILED WITH IPRODIONE OR PIRIMICARB

BY

KANGPING ZHOU ©

A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfillment of the requirement for the degree of MASTER OF SCIENCE

IN

CLOTHING AND TEXTILES

DEPARTMENT OF HUMAN ECOLOGY

EDMONTON, ALBERTA

FALL, 1993

ISBN 0-315-88357-X

UNIVERSITY OF ALBERTA

RELEASE FORM

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TITLE OF THESIS: DECONTAMINATION BY LAUNDERING OF TEXTILES SOILED WITH IPRODIONE OR PIRIMICARB

DEGREE: MASTER OF SCIENCE

YEAR THIS DEGREE GRANTED: 1993

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Dedicated to

My Dad Mr. Zhou Jihua and Mom Mrs. Cao Huiying

UNIVERSITY OF ALBERTA

FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned have read, and recommend to the Faculty of Graduate Studies and Research for acceptance, a thesis entitled DECONTAMINATION BY LAUNDERING OF TEXTILES SOILED WITH IPRODIONE OR PIRIMICARB submitted by Kangping Zhou in partial fulfillment of the requirements for the degree of Master of Science in Clothing and Textiles.

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ABSTRACT

This study contributes to the development of laundering procedures to decontaminate work clothing soiled with pesticides. Such clothing may cause health problems through dermal absorption or inhalation of the contaminant.

Two fabrics, 100% cotton and 65/35 polyester/cotton, which are representative of fabrics used in protective clothing worn by pesticide applicators, were used in this study. Two wettable powder pesticides widely used in Alberta greenhouses, the fungicide iprodione (49.4% active ingredient) and the insecticide pirimicarb (50.7% active ingredient), were used at the recommended concentrations for spraying to contaminate the fabrics. Specimens were contaminated using a digital micropipette, then laundered in a Launder-Ometer after one of the following pre-laundering conditions: no pre-treatment, Spray 'n Wash® pre-treatment, or Javex® chlorine bleach pre-treatment. The laundering cycle included washing at 50°C, and two rinses at 40°C. Laundered and unlaundered specimens were quantitatively analyzed for pesticide residues to the milligram level using HPLC.

There are no significant differences in percent iprodione and pirimicarb residues remaining after laundering between cotton and polyester/cotton specimens. Spray 'n Wash® or bleach pre-treatment caused an effective reduction in iprodione or pirimicarb residue remaining in specimens. Regardless of the pre-treatment, less than 1% iprodione or

pirimicarb residue remained on the two types of fabrics after laundering. Due to extra expense, time, and energy conservation concerns, a single wash in warm water (50°C) is recommended for removing dilute iprodione or pirimicarb residues from fabrics. There are several possible mechanisms for the removal of residues during laundering. Wettable powder pesticides tend to remain on the surface of the fabric and can be removed by agitation. Pesticide water solubility may be increased during warm wash cycles. Combined effects of pesticide, fabric, and pre-treatment on residue removal by laundering have also been found.

After pirimicarb-contaminated fabrics were exposed to air circulation for one day, about 32% pirimicarb residues "dusted off" into the air. This implies that much of pirimicarb residue remain on the surface of specimens. There are potential risks for greenhouse workers wearing pesticide-soiled clothing since inhalation is a common means of exposure, especially in limited-space greenhouses.

ACKNOWLEDGMENTS

I wish to express my sincere appreciation to my supervisor Dr. Nancy Kerr for her guidance, advice, and encouragement throughout my graduate study, and to Dr. Margaret-Ann Armour for her valuable advice on pesticide residue analysis using high performance liquid chromatography (HPLC). I am especially indebted to Dr. Katherine Rigakis for her enthusiasm, encouragement, assistance, dedication, and friendship during my graduate study and research, which makes my study and life here very enjoyable and unforgettable. I would also like to thank Dr. Betty Crown for her valued interest, comments, and suggestions.

My heartfelt appreciation is extended to Alberta Occupational Health and Safety Heritage Program, without whose financial assistance my graduate studies here would not be possible.

A special thank-you goes to Carolyn Nelson for her assistance in analyzing pesticide residues, Terry Taerum for his help on statistical analysis, and many fellow Clothing & Textiles graduate students for their cooperation, companionship, and friendship. Last but not least, I would like to express my deepest appreciation and gratitude to my parents, Mr. Zhou Jihua and Mrs. Cao Huiying, for their always unending understanding, encouragement, support and love throughout my graduate study and life.

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CHAPTER 1 INTRODUCTION

Justification

Pesticides have been widely used in agriculture, forestry, and the greenhouse industries as well as in household gardens. They are chemicals used to destroy insects, fungi, weeds, bacteria, mildew, rodents, algae, viruses, etc. The use of pesticides, however, has been closely associated with hazards to those people who manufacture, deliver, mix, load, and apply them. The hazards include acute and chronic toxicity. The symptoms such as headache, skin irritation, nausea, blurred vision, vomiting, sterility, genetic mutations, birth defects, and some types of cancer range from mild to life threatening (Rigakis, Kerr, Crown & Eggerston, 1987; Laughlin, 1993). Chronic effects are of particular concern as there are no immediate symptoms or signs of poisoning until many years later. In a recent study in Saskatchewan, McDuffie, Semchuk, Olenochuk, and Senthilslvan (in press) found that for some types of cancer (non-Hodgkin's lymphoma, soft tissue sarcoma, skin cancer, lip cancer, prostate cancer, and multiple myeloma), farmers are at a higher risk than the non-farming population.

The greenhouse industry in Alberta has been growing at a rate of 4% annually. There are over 360 commercial greenhouses in the Province of Alberta with over 1200 workers generating over $12 million from sales (Shaw & Willcox, 1988). The use of pesticides in the greenhouse industry presents a particular hazard because they are used in a limited space under hot and humid conditions which enhance direct or indirect dermal absorption of pesticides. Therefore, greenhouse workers have a greater potential risk of exposure to pesticides. In a survey of pesticides used in Alberta greenhouses, 4 out of 28 respondents had experienced pesticide-related illness (Shaw & Willcox, 1988).

It was reported that dermal absorption accounts for 87% of the total human pesticide absorption (Wolfe, 1973). Wearing protective clothing can reduce the risk of pesticide exposure. Work clothing contaminated with pesticides, however, must be thoroughly cleaned prior to reuse; otherwise, pesticide residues which remain in the fabrics may be absorbed dermally. The development of procedures to adequately decontaminate fabrics soiled with pesticides, therefore, becomes essential.

During the past 3 decades, researchers have been using various methods such as laundering, heat, microwaves, ozone, ultraviolet light, dry cleaning, or volatilization in pesticide residue decontamination studies. Much work has been done on decontamination by laundering. As pesticides belong to many different chemical classes, and there are many different formulations and concentrations, no one laundry protocol is successful for all pesticide removal.

In a survey of pesticides used in Alberta greenhouses, 18 out of the 28 respondents used pirimicarb, and 9 used iprodione. Pirimicarb is an insecticide used to control aphids, pea aphids, green peach aphid, and buckthorn aphid on various crops. It is particularly widely used to control aphids on chrysanthemums produced in greenhouses. In Ontario, they represent 22% of flower sales and are the largest sector of this industry (Archibald, Solomon & Stepheson, 1992). Iprodione is a fungicide used to control disease in lettuce, ornamentals, peppers, tomatoes, soft fruit, onions, seed crops, flower crops, and potatoes. Only wettable powder formulation is available in Alberta for both iprodione and pirimicarb. Through an extensive literature search, no decontamination studies have been found to date on work clothing contaminated with the fungicide iprodione or the insecticide pirimicarb. Hence, these two pesticides have been chosen for study.

Purpose

The purpose of this study was to determine effective laundry practices for the removal of two pesticides, iprodione and pirimicarb, from apparel fabrics. This required the development of analytical techniques to extract and measure the pesticide residues which remain in the fabrics.

Objectives

The specific objectives were:

1. To evaluate the effectiveness of different pre-laundering conditions (no pre-treatment, Spray 'n Wash®,

Javex® chlorine bleach soak) in removal of iprodione and pirimicarb from fabrics commonly used for protective clothing.

2. To determine the effect of fabric of different fiber content (100% cotton and 65/35 polyester/cotton) on removal of iprodione and pirimicarb.

3. To determine the effect of the functional groups of the pesticides on residue removal.

4. To develop analytical techniques to extract and measure iprodione and pirimicarb residues using high performance liquid chromatography (HPLC).

Null Hypotheses

To meet the above objectives, the following null hypotheses were tested.

1. There will be no significant interactions among the three independent variables, type of pesticide, fabric, and pre-laundering conditions.

2. There will be no significant difference between iprodione and pirimicarb in percent residue remaining after laundering.

3. There will be no significant difference between 100% cotton and 65/35 polyester/cotton fabrics in percent residue remaining after laundering.

4. There will be no significant difference in percent residue remaining after laundering among different pre-

laundering conditions (no pre-treatment, Spray 'n Wash® pre-treatment, and chlorine bleach pre-treatment).

Definitions

The following definitions were used in this study:

Pesticide: a general term for a wide variety of chemical compounds which are used for controlling, preventing, destroying, repelling, or mitigating any pest (Ware, 1978).

Fungicide: a chemical substance applied to seed, roots, or foliage rendering the plant resistant to fungal attack (Worthing & Walker, 1983).

Insecticide: a chemical substance used mainly against insect pests (Worthing & Walker, 1983).

Organochlorine: an organic compound containing chlorine, such as methyl chloride. Organochlorines are among the most persistent pesticides (World Book Dictionary, 1977).

Carbamate: a salt or ester of carbamic acid (World Book Dictionary, 1977).

Wettable Powder: a chemical that is mixed with water and sprayed onto plants (World Book dictionary, 1977).

Contaminate or Spike: in this study, refers to the addition of pesticide to fabrics using a micropipette.

Decontaminate: in this study, refers to the removal of pesticide soil from fabrics by laundering.

High Performance Liquid Chromatography (HPLC): a technique for separating and analyzing mixtures by liquid chromatography. As high pressure is used to move the mobile phase (a liquid) through the column, it is sometimes referred to as high pressure liquid chromatography (Meyer, 1988).

Assumptions

1. The diluted pesticide concentrations used in this study are representative of those used in Alberta greenhouses.

2. The contamination procedure approximates a liquid pesticide splash to which workers applying pesticides in a greenhouse may be exposed.

3. The fabrics in this study are representative of the fiber content of work clothing worn by pesticide applicators in the greenhouse.

4. The laundry procedure in this study approximates the laundry cycle of an automatic home washing machine.

Delimitations and Limitations

1. Only two pesticides, the fungicide iprodione and the insecticide pirimicarb, representing two chemical classes, were investigated.

2. Only one pesticide formulation, wettable powder, was used for both pesticides.

3. Only one pesticide dilution, that recommended by the

manufacturer, was used for each pesticide.

4. Only two fabrics, 100% cotton and 65/35 polyester/cotton, were used.

CHAPTER 2 LITERATURE REVIEW

The literature review is divided into six sections. In the first section, health problems associated with pesticide use will be reviewed; then in the second section, pesticide parameters affecting the removal of pesticide residues by laundering (chemical class, formulation, and pesticide concentration) are summarized. In the third section, the effects of textile substrate (such as fiber content, yarn and fabric structure, and finishes) on removal of pesticide residues by laundering are discussed. In the fourth section, the effect of refurbishment factors (pre-treatment, detergent type and concentration, wash water temperature, and multiple launderings, etc.) on removal of pesticide residues by laundering are presented. In the fifth section, structures and properties of both iprodione and pirimicarb are introduced. Finally, in the last section, a brief summary is presented.

Health Problems Associated with Pesticide Use

The use of pesticides to control crop diseases and increase agricultural production was initiated in the 1940's. In the 1950's and early 1960's, tremendous progress in pesticide application technology was achieved. Since the late 1960's, with the intensive use of pesticides, much attention has been paid to the impact of pesticides on the environment and on human health and safety (Ragsdale & Kuhr, 1987).

Pesticides have the potential to affect the health of both human beings and animals if they are improperly used or in case of an accident. Pesticide poisoning can be either acute or chronic, although not every pesticide gives all symptoms. Acute effects develop relatively quickly after exposure to pesticides. The acute symptoms of pesticide poisoning can be mild, moderate, or severe. The mild symptoms often are not recognized as they are similar to flu symptoms. Some of the mild symptoms include nausea, headache, tightness of chest, loss of appetite, and stomach cramps. The moderate symptoms are more obvious than the mild ones, such as trembling, muscular incoordination, excessive salivation, difficulty in breathing, vomiting, diarrhoea, eye watering, rapid pulse, and coughing. The severe symptoms are more specific, for example, difficulty in breathing, convulsions, fever, intense thirst, coma, and even death (Crop Protection with Chemicals, 1992). The chronic symptoms of pesticide poisoning occur months or years after exposure, and probably exposure to low doses of mildly toxic pesticides is one of the reasons. The symptoms include peripheral neuropathy, sensitization, carcinogenesis, impaired immunity and immunopathies, cancer risks to brain, heart, liver, kidney, lung, and blood, etc. (Ragsdale & Kuhr, 1987). It is estimated that more than 45,000 human poisonings due to pesticides occur every year all over the world.

Pesticides can enter the human body through three routes:

respiratory, oral, and dermal. Many researchers have concluded that dermal exposure to pesticides is the major route, as skin is the largest organ of the human body (Wester & Maibach, 1985; Libich, To, Frank & Sirons, 1984; Adamis et al., 1985). Wolfe, Durham & Armstrong (1966) found less than 1% of total pesticide exposure was the result of inhalation. Inhalation occurs as a result of breathing pesticides in the form of fumes, dusts, or spray mists. Oral absorption may occur when pesticide users eat, drink, or smoke without washing their hands. Fenske (1986) and Archibald et al. (1992) confirmed that substantial dermal exposure occurred beneath work clothing by using quantitative fluorescent tracer analysis in greenhouses. In a study of pesticide exposure in greenhouses, Admis et al. (1985) measured respiratory exposure using a personal sampler and pesticide deposition on skin using 12-layer gauze pads fitted to different parts of the body. Dermal exposure differed significantly with the part of pesticide applicator's body which was exposed. The exposure of hands, arms, and legs was found to be the greatest. Dermal exposure was several times higher than respiratory exposure. Maibach, Feldmann, Milby, and Serat (1971) investigated the rate at which different parts of the body absorb pesticides. They found that if the absorption rate in the area of the forearm is 1.0, the absorption rate in other parts of the body would be : scalp 3.7, forehead 4.2, ear canal 5.4, abdomen 2.1, palm 1.3, genital area 11.8, and ball of foot 1.6. The genital area and the head absorb the greatest amount of pesticide.

Skin exposure to pesticides can occur by direct handling of pesticides, by indirect transfer from contaminated work clothing or equipment, or by indirect transfer to other clothing from contaminated work clothing during laundering. Some pesticides may not be absorbed by the skin, but still cause skin problems such as redness, blisters, or dry scaliness which may develop into serious skin eczema and dermatitis problems. Toxic chemicals that are absorbed through the skin are disseminated by the blood stream to the whole body (Niles, 1985). Dermal exposure can be significantly reduced by the use of appropriate protective equipment and appropriate laundering procedures that remove pesticide residues in contaminated work clothing (Nelson et al., 1988). An adult male whose clothing was contaminated with methyl parathion died because the clothing was not adequately decontaminated before wearing again (Southwick, Mecham, Cannon & Gortatowski, 1974). Decontamination of work clothing soiled with pesticides is essential before re-use.

Pesticide Parameters in Residue Removal

Research on the removal of pesticide residues from contaminated work clothing has shown that the efficacy of decontamination varies significantly among pesticides from different chemical classes, formulations, and concentrations; however, predictions or generalizations on the ease of residue removal only based on chemical class, formulation or concentration should be avoided as the interactions are complex and generalizations cannot be made from one pesticide to another.

Keaschall, Laughlin and Gold (1986) found differences in amounts of residue remaining in fabrics after laundering among pesticides from different chemical classes. Eleven pesticides from three different chemical classes were studied. Contamination by the organochlorine pesticides resulted in the largest residues and that by carbamates the smallest residues. The results varied greatly among the organophosphate pesticides. Pesticide mixtures have been found to be more difficult to remove than a single pesticide (Finely et al., 1974). Chiao-Cheng (1984) found the two carbamates, carbofuran and methomyl, were each readily removed from cotton and polyester/cotton by laundering.

Pesticide formulation is an important factor in residue removal by laundering. Commercial pesticides are a mixture of pesticide, carrier, surface-active agents, and other ingredients. Some of the formulations widely used in agriculture and the greenhouse industry include emulsifiable concentrate, encapsulated, wettable powder, dust, and granule (Speight, 1980). Among these, emulsifiable concentrate, encapsulated, and wettable powder are the most frequently used. All the above formulations have the potential to be toxicological hazards and some of them may have the potential to be flammable hazards as well. Easley and co-workers (Easley, Laughlin, Gold, & Tupy, 1981; Easley, Laughlin, Gold, & Hill, 1982) evaluated the ease of residue removal of three different formulations of methyl parathion (emulsifiable concentrate, encapsulated, and wettable powder). They found that residue from encapsulated and wettable powder formulations was far less than that of emulsifiable concentrate. In addition, more variation in residue was found for the wettable powder than for the other two formulations. They also reported that the wettable powder formulation was the easiest to remove from contaminated fabric and also the easiest to be transferred to clean fabric if contaminated and non-pesticide contaminated clothing are washed together, due to the particulate nature of their composition. Raheel and Yu (1993) reported wettable powder and flowable liquid formulations of carbaryl and atrazine were efficiently removed from fabrics after laundering. Kim and Wang (1993) found that at least 99% of atrazine in granule or dust formulation was removed by laundering.

In addition to the pesticide chemical class and formulation, concentration also significantly influences the ease of residue removal by laundering. Diluted methyl parathion (1.25% active ingredient) was readily removed by washing, but the concentrate (54% active ingredient) was found difficult to remove by laundering. Even after 10 laundry cycles, 33.3% methyl parathion residue remained (Laughlin, Easley, & Gold, 1985). Crown, Armour and Kerr (1993) reported that it was difficult to remove concentrated full strength commercial malathion and chlorpyrifos from fabrics by laundering. This confirmed the work of Laughlin et al. (1985). It appears that greater protection for pesticide users is required when dealing with concentrated pesticide solutions. Protective workwear which has been contaminated accidently with the concentrated pesticides such as methyl parathion, malathion, and chlorpyrifos should be replaced rather than laundered and re-used.

The Textile Substrate in Residue Removal

The textile substrate (fiber content, yarn and fabric structure, and finish) influences not only pesticide retention in the fabric and penetration through the fabric, but also the ease of pesticide residue removal.

Cotton and blends of polyester and cotton are the most frequently used fibers in work clothing. Cotton is a natural cellulose fiber with medium strength, low elongation, high absorbency and low resiliency; polyester is a synthesized thermoplastic polymer that is strong, highly resilient, dimensionally stable, hydrophobic, and oleophilic. The effect that fiber content has on penetration and residue remaining after laundering has been studied by a number of researchers. Easter (1982) found a significant difference in residue removal among different fabrics. Captan® residue was easier to remove from nylon fibers than from cotton fibers. This is due to the fact that more particulate soils of Captan® accumulate on the curled ribbon-like cotton fibers than on smooth surfaced nylon fibers. Guthion® residue, on the contrary, was easier to remove from cotton fibers because the emulsifiable concentrate containing Guthion® has more affinity for oleophilic nylon fibers than oleophobic cotton fibers. Raheel (1988) investigated laundering effectiveness of several fabrics of different fiber content, cotton, polyester, nylon, acrylic, and spunbonded olefin. She concluded that fiber content in general did not influence after-laundry retention of carbaryl or atrazine. Lillie, Livingston, and Hamilton (1981) observed that 100% cotton fabric afforded better protection and greater resistance to penetration than 100% polyester fabric, but there were no significant differences in the amount of chlordane, diazinon, carbaryl, and prometon residue remaining in the two fabrics after laundering. Nelson et al. (1992) investigated the removal of 15 pesticides from six chemical classes from fabrics of two different fiber types, 100% cotton and 50/50 polyester/cotton. They found there were significant differences between fabrics in removal of carbaryl, cypermethrin, atrazine, and trifluralin. The percent remaining of carbaryl and atrazine was higher in cotton; however, the percent remaining of cypermethrin, deltamethrin and trifluralin was higher in polyester/cotton blends. The removal mechanisms are influenced by many factors such as fiber type, pesticide properties, physical entrapment, penetration, etc.

Fabrics differ in fabric geometry, mass, thickness and count. Each of these factors affects pesticide retention, penetration, and removal by laundering. A fabric can be constructed by various methods: woven, knitted, stitch-bonded, tufted, etc. (Joseph, 1986). Woven fabrics are still the most widely used for protective clothing; however, non-woven disposable garments which require no laundering are now on the market. They are, however, more limited in size and availability than woven work clothing, and because they must be discarded after use, they do add to the expense of the farm operation.

Finishes affect fabric performance, maintenance, durability, appearance, and serviceability. Soil or stain repellent finishes, durable press finishes, soil release finishes, and water repellent finishes, may significantly affect pesticide retention and/or penetration, as well as removal of residue from contaminated fabrics by laundering. Laughlin and Gold (1987) found a soil repellent finish was a significant factor in methyl parathion residue removal through laundering practices, as the soil repellent finish provided protection by limiting absorption of pesticide into the specimens. They also found methyl parathion was more difficult to remove by laundering from durable press finished fabrics than from unfinished samples, since a durable press finish increases a fabric's hydrophobicity. Laughlin, Lamplot, and Gold (1987) found a single application of starch to fabrics was not effective in lowering chlorpyrifos left after laundering. However, Sagan and Obendorf (1988) observed that the application of a heavy level of starch as a temporary finish facilitated removal by laundering of methyl parathion residue from 100% cotton and 65/35 polyester/cotton fabrics.

Refurbishment Factors in Residue Removal

The earliest studies on the laundering of pesticide contaminated work clothing were conducted by Finley and co-workers at the Louisiana Agriculture Experimental Station (Finley & Rogillio, 1969). Since then, extensive and excellent research work has been done in this area. A number of researchers have studied factors such as pre-treatment, wash water temperature, detergent type and concentration, multiple launderings, the use of laundry aids, water hardness, and pH of wash or rinse water.

Pre-treatment is often a very effective method of decreasing pesticide residues which are difficult to remove. Olsen, Janecek and Fleeker (1986) found a pre-rinse removed most of the paraquat residue and was the most effective individual procedure in laundering paraquat contaminated clothing. They reported that increasing the pre-rinse time had no effect, but increasing the volume of water in the pre-rinse step did. Keaschall, Laughlin, and Gold (1986) found a pre-wash surfactant pre-treatment was more effective than laundering alone in removing residue of 11 pesticides from 3 chemical classes. Research at the University of Alberta demonstrated that the use of a Spray 'n Wash® pre-treatment was effective for the removal of triallate, trifluralin, and deltamethrin (Rigakis, Martin-Scott, Crown, Kerr & Eggerston, 1987). Although Raheel and Yu (1993) reported that a pre-wash treatment did not significantly enhance residue removal of carbaryl or atrazine, both pesticides were readily removed in the wash.

Perkins et al. (1992) found the most effective pre-treatment to remove chlorpyrifos was a 3-hour Javex® chlorine bleach soak (0.03% residue remained). A Javex® oxygen bleach soak pre-treatment is also effective for removal of chlorpyrifos (3.3% residue remaining), but could be too costly to be practical. The most effective non-bleach pre-treatment for chlorpyrifos removal was Spray 'n Wash® (8.1% residue remaining). If given only one wash, without any pre-treatment, 44.7% chlorpyrifos residue remained in the fabrics. Park (1986) found that a simulated sunlight exposure as a pre-treatment prior to laundering improved removal of some pesticides on Gore-Tex® fabrics.

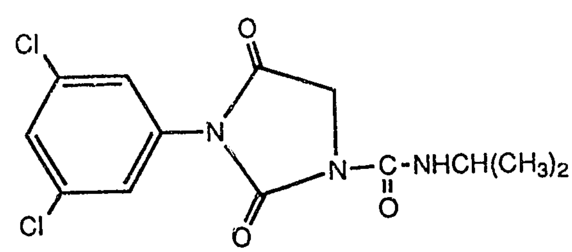
Wash temperature is an important factor in decontamination. Laughlin, Easley and Gold (1985) reported that no significant difference in the ease of removal of methyl parathion residue was found between a 60°C and 49°C wash, but a 30°C wash resulted in higher residues. Kim and Wang (1992) found that a hot wash (60°C) was more effective than a warm wash (49°C) in removing atrazine residues in granular or dust formulations. The wash water temperatures studied were mostly warm (49°C) and/or hot (60°C), which are in the range of temperatures recommended for Tide®, AATCC 124 detergent, or heavy duty liquid detergents (Laughlin & Gold, 1988). Lillie, Hampson, Nishioka, and Hamilton (1982) studied the removal of diazinon and chlorpyrifos from cotton fabric by laundering at temperatures of 30°C, 43°C, and 60°C. They noted less pesticide residue was left with increasing temperature when detergent or detergent and bleach were used in wash water. When detergent or bleach products were not used, pesticide residue removal did not increase when temperature increased. Due to energy conservation concerns, cool wash temperatures are becoming more popular; however, for most pesticides studied, a cool wash is not recommended. One exception to this generalization has been found. Samuel and Guillot (1992) reported that even when using cold water (5°C) without detergent, more than 95% of the herbicide glyphosate could be removed from contaminated work clothing. This is due to the high solubility of glyphosate in water.

Laundry detergents contain surface active agents, solids, and water. The four major classes of surface active agents are anionic, cationic, nonionic, and amphoteric. The majority of commercially available laundry detergents are anionic or nonionic. Chiao-Cheng (1988) found no significant differences among three detergents, granulated Tide® (anionic), heavy duty liquid All® (nonionic) and Wisk® (nonionic), used in removing residues of carbofuran and methomyl. Easley et al. (1982) investigated four detergents, nonionic heavy duty liquid, anionic phosphate, high phosphate, and carbonate, in decontamination of methyl parathion from fabrics. No significant differences were found among the four detergents in the efficacy of residue removal. Higher detergent concentration results in a larger quantity of surface active agent being present. This aids in the removal of residues of the pyrethroids, cypermethrin and cyfluthrin (Laughlin and Gold, 1991). The authors noted, however, that at the higher wash temperature (60°C), increasing the detergent concentration is not helpful in removing residues of methyl parathion.

Multiple launderings are effective in decontaminating pesticides which are difficult to remove. Rigakis et al. (1987) reported that 18.2% deltamethrin, 23.0% trifluralin, and 48.2% triallate remained in cotton fabric after a single wash cycle without pre-treatment, however, an additional wash cycle reduced the pesticide residues to 10.8% deltamethrin, 16.3% trifluralin, and 35.2% triallate. If a Spray 'n Wash® pre-treatment is done prior to the multiple laundering, the residues are reduced further. Laughlin et al. (1985) reported that a third laundry cycle lowered the residue of methyl parathion to less than 1%. Finley et al. (1979) found even three laundering cycles could not effectively remove methyl parathion in a mixture with toxaphene and DDT. Ten wash cycles were not effective in removing residue from concentrated methyl parathion contaminated work clothing (Laughlin et al., 1985). Multiple launderings must be evaluated along with other factors such as energy use and water conservation. No laundering should be done if work clothing has been contaminated by a spill of concentrated pesticides, for example, methyl parathion, malathion, and chlorpyrifos. Rather, the clothing should be discarded.

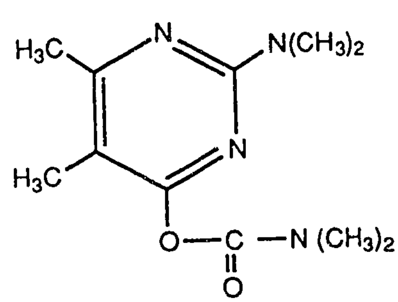
Iprodione and Pirimicarb

The fungicide iprodione is the common name for 3-(3,5-dichlorophenyl)-N-(1-methylethyl)-2,4-dioxo-1-imidazolidinecarboxamide. Its formula is $C_{13}H_{13}Cl_2N_3O_3$ with a chemical structure as follows:



Iprodione was introduced by Rhône-Poulenc Agrochimie with the trade name "Rovral". Commercial iprodione is a dull yellow color, whereas pure iprodione is in the form of colourless crystals with a melting point of 136°C. Its solubility in water (20°C) is 13 mg/L and in acetone is 300 g/L. It can be degraded by UV light, especially when dissolved in water. Iprodione is commercially available as a wettable powder formulation with 50% active ingredient. It is particularly effective against fungi on cereals, fruit, oilseed rape, rice, vegetables, and vines (Worthing and Walker, 1983). The use of iprodione is authorized, or is in the process of registration, for various crops and in various countries. Its toxicity is low with an LD_{50} of 3500 mg/kg for rats. Some analytical research work has been done on this fungicide and various analytical methods have been used to determine residual quantities on fruit and vegetables in the environment (Cabras, Dianna, Meloni, Pirisi, Pirisi, 1983) In the research of Cabras et al. (1983), HPLC was used to determine the pesticide residue in wines. They found that light petroleum was the best extraction solvent and mobile phase was acetonitrile:water (55:45) was used as a mobile phase.

The insecticide pirimicarb is the common name for 2-(dimethylamino)-5,6-dimethyl-4-pyrimidinyldimethylcarbamate. Its formula is $C_{11}H_{18}N_4O_2$ with a chemical structure as follows:



Pirimicarb was introduced by ICI Plant Protection Division with trade names "Pirimor" and "Aphox". Commercial pirimicarb is a blue color, whereas pure pirimicarb is a colourless solid with a melting point of 90.5°C. Its solubility in water (25°C) is 2.7 g/L and in acetone is 4.0 g/L. It can be hydrolysed on heating with acid or alkali. It is commercially available as a wettable powder formulated with 50% active ingredient. It is effectively used as an aphicide in cereals, fruit, ornamentals, and vegetables. Its toxicity is high with an LD_{50} of 147 mg/kg for rats (Worthing and Walker, 1983). Some studies on pirimicarb are applicable here (Archibald et al., 1992; Cabras, Spandedda, Tuberoso, and Gennari, 1989; Oi, Watanabe, and Suzuki, 1980). Oi et al. (1980) used a gas-liquid chromatographic technique to determine the residue of pirimicarb. Acetone was used as an extraction solvent and phthalic acid di-n-decyl ester as an internal standard. The recovery of pirimicarb was found to be 100%. Cabras et al. (1989) used HPLC to separate pirimicarb and its major metabolites. The mobile phase used was water-acetonitrile or phosphate-buffered acetonitrile in various ratios.

Summary

The decontamination of pesticide soiled work clothing is a complicated process with many factors involved. This literature review summarized some of the factors which are important for pesticide residue removal by laundering. Iprodione and pirimicarb were chosen for study because they are widely used in Alberta greenhouses and no laundering decontamination studies have been found to date on the two pesticides. One hundred percent cotton and 65/35 polyester/cotton were chosen because they are most widely used in work clothing. The Spray 'n Wash® pre-treatment followed by laundering was effective in removing residues of many pesticides including triallate (carbamate) from work clothing (Rigakis et al., 1992; Nelson et al., 1992). Chlorpyrifos (organochlorine) was effectively removed by using a Javex® chlorine bleach pre-treatment (Perkins et al., 1992). These two pre-treatments were chosen as pre-laundering conditions in this study as iprodione is an organochlorinated carboxamide and pirimicarb is a carbamate. They were expected to be effective for iprodione and pirimicarb. This study investigates the decontamination by laundering of fabrics soiled with the two pesticides and evaluates the effects of pesticide, fabric, pre-treatment, and possible interactions among them.

CHAPTER 3 MATERIALS AND METHODS

In this chapter, the experimental design of the study, the selection, sampling, and preparation of fabrics, fabric characterization, labware cleaning procedures, pesticide dilution, fabric contamination, pre-treatment and laundering are outlined. The analysis of pesticide residues by extraction from the fabrics, evaporation of the solvent, and HPLC analysis, and laboratory safety precautions are presented. Finally, the statistical analysis is described.

The Experimental Design

This study is a 2 x 2 x 3 complete factorial design with two runs (see Table 1). The independent variables are type of fabric (100% cotton and 65/35 polyester/cotton), pesticide (iprodione and pirimicarb), and pre-laundering conditions (no pre-treatment, Spray 'n Wash® pre-treatment, and chlorine bleach pre-treatment). The dependent variable is the pesticide residue remaining in a fabric after laundering, as measured by HPLC. Two runs were completed for each pesticide under each set of conditions. For each run, a fresh solution of pesticide was used. A total of 6 specimens were analyzed per fiber type/ laundry treatment condition. The amount of pesticide extracted from both unlaundered control specimens and the laundered ones was expressed in milligrams per specimen.

Table 1

Summary of the Experimental Design

Group	Pesticide	Fabric	Pre-laundering Condition
Group1	Iprodione	Cotton	No pre-treatment
Group2	Iprodione	Cotton	Spray 'n Wash®
Group3	Iprodione	Cotton	Bleach
Group4	Iprodione	Polyester/cotton	No pre-treatment
Group5	Iprodione	Polyester/cotton	Spray 'n Wash®
Group6	Iprodione	Polyester/cotton	Bleach
Group7	Pirimicarb	Cotton	No pre-treatment
Group8	Pirimicarb	Cotton	Spray 'n Wash®
Group9	Pirimicarb	Cotton	Bleach
Group10	Pirimicarb	Polyester/cotton	No pre-treatment
Group11	Pirimicarb	Polyester/cotton	Spray 'n Wash®
Group12	Pirimicarb	Polyester/cotton	Bleach

Fabric Selection, Preparation, and Characterization

The fabrics used in this study were a bleached and mercerized twill weave 100% cotton[1] and 65/35 polyester/cotton obtained from a U.S. mill for the North Central Regional Pesticide Research Project NC-170 "Enhancing Health and Safety Through Textile System"[2]. These fabrics are similar in mass, yarn, and fabric construction to the fiber, weave, and mass commonly found in the work clothing worn by pesticide applicators. The fabrics were unfinished and undyed to minimize potential problems in the extraction, evaporation, and identification of pesticide residues. Before sampling, fabrics were stripped of warp sizing and manufacturer-applied fabric softeners and impurities by washing five times following washing procedure (1) (IV) (Ai) in American Association of Textile Chemists and Colorists (AATCC) Test Method 135-1992, Dimensional Changes in Automatic Home Laundering of Woven and Knit Fabrics (AATCC, 1992).

After stripping and before preparation of specimens, the outer ten percent of each fabric width was removed following American Society for Testing and Materials (ASTM) Test Method D 1682-64, Test for Breaking Load and Elongation of Textile

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[1]Style #423, Testfabrics, Inc., P. O. Drawer O, 200 Blackford Ave., Middlesex, NJ 08846, USA.

[2]A U.S Agriculture Experiment Station Project, now into the third 5-year period (October, 1992 to September, 1997) with participants from universities in Alberta, California, Cornell, Georgia, Illinois, Iowa, Kansas, Maryland, Michigan, North Carolina, Oklahoma, and South Dakota.

Fabrics (Annual Book, 1990). The procedures for fabric preparation are similar to those used in the NC-170 decontamination studies.

Fabric characterization was completed after fabric stripping. Fabric mass (CAN/CGSB-4.2 No.5.1-M90), threads per unit length (CAN/CGSB-4.2 No.6-M89 (ISO 7211/2-1984), Method C), and fabric thickness (CAN/CGSB-4.2 No.37-M87) were determined.

Specimen Sampling and Conditioning

The specimens were cut into 8 x 8 cm squares on the bias to prevent ravelling in laundering. Specimens were randomly numbered using a random number table and stored individually in numbered plastic bags until ready for use. Specimens were used in consecutive order, beginning with the specimens numbered 1,2,3......

Before contamination, specimens were conditioned overnight in a standard atmosphere of 20 ± 2°C and 65 ± 2% relative humidity according to CAN/CGSB-4.2, No.2-M88, Conditioning Textile Materials for Testing, to avoid differences in specimen moisture content influencing the absorption of the pesticide.

Cleaning of Labware

To clean and minimize potential cross contamination, all the labware used in this study was thoroughly cleaned. The labware was first rinsed well with acetone, then washed in Versa-Clean™ detergent solution[3], followed by three rinses using hot tap water, cold tap water, and distilled water. Finally, it was rinsed with acetone again and air dried before re-use.

Pesticide Dilution

The pesticides chosen for this study were the fungicide iprodione (commercial Rovral® produced by May & Baker Canada Inc.[4]) and the insecticide pirimicarb (commercial Pirimor* 50WP produced by Chipman Inc.[5]). Both pesticides were wettable powders, and were stored in glass vials covered with aluminum foil to avoid light degradation. Measured by HPLC analysis, the percentage of active ingredient was found to be 49.4% for iprodione and 50.7% for pirimicarb.

The pesticides were applied to the fabrics at the dilutions recommended on the packages for field use, 1.0 mg/mL (0.049% active ingredient) for iprodione and 0.5 mg/mL (0.025% active ingredient) for pirimicarb. The pesticide suspension was poured into a 500 mL beaker and magnetically stirred during the contamination procedure to keep the pesticide in suspension and avoid settling of the solid to the bottom of

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[3]Fisher Scientific, Nepean, Ontario K2E 7L6, Canada

[4]2000 Argentia Road, Plaza 3, Mississauge, Ontario L5N 1V9, Canada

[5]Stoney Creek, Ontario L8G 3Z1, Canada

the beaker.

Contamination of Specimens

The contamination procedure described by Rigakis et al. (1987) was followed. Galvanized wires covered with aluminum foil were strung from plastic hooks across a fumehood. The foil was discarded after each contamination experiment to protect the wires and prevent potential cross contamination between specimens. Fifteen conditioned test specimens per fabric type were held horizontally by pinning two diagonally opposite corners to the two neighbouring wires. Contamination was done by pipetting 0.5 mL of diluted pesticide to the center of each fabric specimen, using a digital Eppendorf micropipette with disposable tips (Varipette® 4810 supplied by Brinkmann Instruments, Inc.[6]).

The pesticide mixture (0.5 mL) was pipetted into each of three empty 500 mL Erlenmyer flasks to allow the accuracy of the dilution to be tested and to calculate extraction efficiency. Three conditioned specimens of cotton and polyester/cotton were individually placed into 500 mL Erlenmyer flasks and 0.5 mL diluted pesticide solution added to the specimens. The flasks were closed with Teflon-lined screw caps.

The extraction efficiency was calculated as follows:

Extraction Efficiency (%) = 100 x SE / P

[6]One Cantiague Road, Westbury, NY 11590-9974, USA

Where SE = pesticide (mg) in spiked-in-Erlenmyer specimens;

P = pesticide (mg) in pesticide-only specimens.

The specimens contaminated on the lines in the fumehood were allowed to air dry for 24 hours. Three specimens for each fabric were placed individually in labelled 500 mL Erlenmyer flasks and kept as unlaundered controls. The remaining 9 cotton and 9 polyester/cotton specimens were subjected to different pre-laundering conditions and laundering. This contamination procedure was run twice for each pesticide studied.

Laundering Pre-treatments

The contaminated specimens were subjected to three laundry processes: no pre-treatment/one wash, Spray 'n Wash® pre-treatment/one wash, Javex® liquid chlorine bleach soak/one wash. The choice of Spray 'n Wash®, a commercially-available liquid laundry soil/stain remover, produced by Dow Consumer Product Inc.[7], and Javex® chlorine bleach solution produced by Colgate-Polmolive Canada Inc.[8], as pre-treatments were based on previous research work done by Perkins et al. (1992).

Spray 'n Wash® Pre-treatment

For the Spray 'n Wash® pre-treatment process, 1 mL of

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[7]Greenville, SC 29602, USA

[8]Toronto, Ontario M4G 2H6, Canada

this product was applied to the center of the contaminated test specimen using a digital Eppendorf micropipette. After one minute, the Spray 'n Wash® pre-treated specimens were laundered.

Chlorine Bleach Pre-treatment

The bleach soaking pre-treatment outlined by Perkins et al. (1992) was followed. Immediately before use, Javex® liquid chlorine bleach (4 mL) was diluted to 1 L with distilled water at 50°C. Stainless steel canisters were placed in a water bath at 50°C and allowed to equilibrate to this temperature. Into each canister were placed twelve stainless steel round metal disks (3 centimetres in diameter), then 150 mL of the diluted bleach solution was added. The use of twelve metal disks per canister prevented the canister from floating when placed in the bottom of the washing machine for the soaking period. A contaminated specimen was placed in each canister and totally submerged in the chlorine bleach solution. Canisters were set in the bottom of a washing machine filled with 50 ± 2°C tap water and left for 3 hours. This was done in order to duplicate the cool down period of an automatic home washing machine.

Three hours later, the temperature of the washing machine water was measured, the canisters were removed, and the bleach solution was decanted. The soaked specimens were ready to be laundered.

Laundering Process

The laundering process outlined by Perkins et al. (1992) was followed. One specimen and twenty-five stainless steel balls (0.64 centimeter in diameter) were placed in each stainless steel canister. The stainless steel balls provide agitation during the laundering process in the Atlas Launder-Ometer (Model B-5, Type LHD-EF, manufactured by Atlas Electric Devices Co., Chicago, USA) and simulate the mechanical action which occurs in laundering. One hundred and fifty mL of a 0.2% (w/v) powdered Tide® detergent solution at 50°C was poured into each canister. Before the canister lids were closed, Teflon-liners were placed over the rubber gaskets to prevent pesticide absorption. Eighteen specimens of both fiber types which had been subjected to three different pre-laundering conditions (no pre-treatment, Spray 'n Wash®, or chlorine bleach pre-treatment) were washed simultaneously.

The wash consisted of a 12-minute detergent cycle and two rinse cycles. The wash water was decanted from the canisters after the 12-minute detergent cycle. The water temperature of the Launder-Ometer was then lowered to 40°C. Rinse water (150 mL) at 40°C was added to each canister. Distilled water was used in both laundering and rinse steps to reduce water impurities and facilitate pesticide residue analysis. The rinse cycles were of 5 and 3 minutes duration, respectively.

The laundering conditions described were chosen to simulate the single home laundering cycle used by many pesticide applicators in the Province of Alberta. The majority of farm families in Alberta use a 50°C wash and a cool rinse (Rigakis et al., 1987); 56% of farm families surveyed most commonly use Tide® as detergent. After laundering, each specimen was hung vertically on the lines in the fumehood and allowed to drip dry for 24 hours. Specimens were then stored individually in 500 mL Erlenmyer flasks ready for extraction and analysis.

Extraction of Pesticides from Fabrics

The solvent selected for extraction of the pesticide from the fabric and the procedure used were based on preliminary work. The highest extraction efficiency was obtained by using acetone as the extraction solvent.

Pesticide grade acetone (100 mL) was added to each specimen stored in the Erlenmyer flasks. The flasks were clamped onto a mechanical shaker (Burrell Wrist-Action Shaker manufactured by Burrell Corp., Pittsburgh, PA, USA).

After the initial 30 minute shaking, the acetone was decanted into 500 mL round-bottomed flasks. These flasks were then capped with cork stoppers and wrapped with Parafilm "M" to avoid evaporation. Another 100 mL of acetone was added to each Erlenmyer flask and the process was repeated. Finally, each fabric specimen was rinsed with 75 mL of acetone. The acetone extracts for each specimen were combined. Therefore, for each specimen, the total volume of extracting acetone was

275 mL.

Evaporation of Extracted Solutions

After extraction, each round-bottomed flask was clamped to a rotary vacuum evaporator (Büchi Rotavapor, No. 13859, made in Switzerland). The flask was immersed in a temperature-controlled warm water bath. The temperature was kept at about 30°C to facilitate evaporation. The solvent was reduced to a volume of 2 - 4 mL. The remaining solution was transferred to a 25 mL round-bottomed flask. The 25 mL flask was thoroughly rinsed 5 times with small quantities of acetone. The rinses were added to the 25 mL round-bottomed flask and the liquid evaporated. The flasks were stored in a refrigerator until the contents were analyzed.

HPLC Analysis

The flasks containing pesticide residues were removed from the refrigerator and allowed to come to room temperature. This took approximately 30 minutes. The residue was dissolved either in acetonitrile (iprodione) or 50:50 acetonitrile: buffer solution (pirimicarb) for injection into the HPLC. A 1 L 0.01 M phosphate buffer solution was prepared by mixing 1.3609 g KH_2PO_4, 5 mL glacial acetic acid, 1.1 mL triethylamine, and distilled water.

The HPLC was used to analyze pesticide residues. The system used a SSI 220 B HPLC pump, automatic Rheodyne injection valve, a 25 cm x 2.1 mm ID Supercosil-18-DB analytical column covered with fiberglass and cotton insulation, a guard column to protect the analytical column and to remove impurities from the injected sample solutions, SSI 500 detector of variable UV/Visible light, and a computerized integrator (HP3396A) to record the retention time and peak areas of samples and to print the chromatogram. The conditions for the chromatography of iprodione and pirimicarb were optimized from the research of Cabras and co-workers (1983). In pirimicarb analysis, it was recommended by Supelco Canada, that 8 mM triethylamine be used in the buffer solution to solve peak tailing problems. Calibration graphs were obtained by using a series of dilutions of pure iprodione or pirimicarb of varying concentration. The HPLC was recalibrated once a month or more frequently as needed. In order to obtain an accurate and reliable calibration graph, pure iprodione and pirimicarb (PESTANAL® supplied by Caledon Labs[9]) were weighed using a microanalytical balance. A series of diluted solutions was prepared and concentrations were measured by HPLC. A calibration graph was obtained based on the results. A known-percentage-of-pesticide solution was used to check the calibration graph obtained. The optimal HPLC conditions for iprodione and pirimicarb are given in Appendix 2.

The mobile phase for both iprodione and pirimicarb analysis was filtered before use to degas. Double distilled

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[9]14615-124th Avenue, Edmonton, Alberta T5L 3B2, Canada

water was used to prepare the mobile phase solution for both pesticides to reduce impurities and to obtain stable baselines. The detection limits of the instrument were measured to be 1.7 x 10^{-6} mg/mL for iprodione (3.5 x 10^{-6} mg per specimen) and 2.2 x 10^{-6} mg/mL for pirimicarb (5.5 x 10^{-7} mg per specimen). A standard solution was injected before and after duplicate specimen runs to confirm the retention time of pesticide peaks. An internal standard solution, dibutyl phthalate, was employed for the iprodione HPLC analytical work, but not for pirimicarb. The iprodione residues were measured by comparing the areas of the peaks due to iprodione to those of an internal standard. The amount of pirimicarb remaining was measured directly from the area of the peak due to the pesticide. Two analyses were made for each specimen solution and the results averaged. Each time, a 100 μl sample of the solution was injected using a Hamilton 250 μl syringe.

Laboratory Safety Precautions

In order to minimize exposure of the researcher to the pesticides, safety precautions were taken throughout the experiment. A laboratory coat, a pair of safety glasses and disposable gloves were always worn when mixing and handling the pesticides and working with the contaminated specimens. Manipulation of chemicals was done in a fumehood.

Statistical Analysis

To test the null hypotheses, statistical analysis of the data was performed with the data for pesticide residues remaining on the fabrics expressed as a percentage of pesticide on the unlaundered controls. For those samples where the pesticide was below the detection limit (N.D), zero was used in the statistical analysis. A computer software package SPSS® for Windows™ (SPSS Inc.[10]) was used to perform the statistical analysis. The significance level for all hypothesis testing was set at 0.05.

Analysis of variance (ANOVA) was employed to test the main effects of each independent variable (type of fabric, pesticide, and pre-laundering conditions), two-way interactions between pairs of independent variables, and three-way interactions among the independent variables. The Kolmogorov-Smirnov Goodness of Fit Test was run to test the normality of the data, and the Levene Test was performed to test homogeneity-of-variance of the data. Because the assumptions of ANOVA (normality and homogeneity-of-variance of the data) were violated, as revealed by the above tests, a nonparametric Robust Regression analysis was employed to analyze the data.

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[10]444 N. Michigan Avenue, Chicago, Illinois 60611, USA

CHAPTER 4 RESULTS AND DISCUSSIONS

In this chapter, fabric characterization, selection of the extraction solvent, extraction efficiencies for iprodione and pirimicarb, and mean values of iprodione and pirimicarb remaining in fabrics after laundering are reported. A nonparametric Robust regression statistical model is established. Each null hypothesis is re-stated, followed by the result of statistical analysis which leads to acceptance or rejection of the null hypothesis. The interactions and the main effects of independent variables are discussed based on statistical analysis. Possible mechanisms for the removal of pesticide residues by aqueous laundering are proposed.

Fabric Characterization

Fabric characterization (fabric mass, threads per unit length, weave, and fabric thickness) is reported in Table 2. Both fabrics were undyed and without functional finishes. The 100% cotton fabric was mercerized.

Both fabrics are twill weaves with similar mass, thickness, and thread counts. It is not possible to find fabrics that are identical in mass, thickness and thread count when there is a difference in fiber content. Workwear of 100% cotton usually has a higher mass than polyester blends with cotton, partly because of the lower specific gravity of the polyester fiber and partly because a heavier yarn is used in the 100% cotton fabric in order to increase its durability. It is important that both fabrics are similar in fabric characterization; if they are not, then fabric geometry can become an intervening variable which affects the pesticide residue in the fabric and can lead to erroneous conclusions.

Extraction Solvent and Efficiency

The mean values of extraction efficiencies for iprodione and pirimicarb are listed in Table 3. The extraction solvent acetone is inexpensive, very easy to evaporate, and three 30-minute shaking periods resulted in high pesticide recovery. A high extraction efficiency indicates the solvent is able to remove all the pesticide or nearly all the pesticide in the specimen. If the extraction efficiency is low, pesticide remains in the fabric, and it might be concluded erroneously, that decontamination through laundering was effective, whereas in reality pesticide has remained, undetected, in the fabric.

Loss of Pirimicarb from Unlaundered Specimens

It was noted that the unlaundered control specimens contaminated with pirimicarb had only 68% pesticide residue remaining on the specimens after contamination and air drying for 24 hours in the fumehood. An additional set of experiments was done to determine whether the pesticide loss was due to a breakdown of the pirimicarb or whether the pesticide was

Table 2

Fabric Characterization

Fiber Content	Mass[a] g/m²	Thickness[b] mm	Weave[c] W x F	Threads[d]/cm W x F
100% Cotton	305	0.8	3 x 1	45 x 23
65/35 P/C	270	0.7	2 x 1	34 x 19

[a]CAN/CGSB-4.2 No.5.1-M90. [b]CAN/CGSB-4.2 No.37-M87. [c]Twill weave. [d]CAN/CGSB-4.2 No.6-M89 (ISO 7211/2-1984), Method C.

Table 3

Acetone Extraction Efficiency of Iprodione and Pirimicarb from Fabrics

Pesticide Name	Acetone Extraction Efficiency (%)[a] Cotton (std.dev.)	Poly/Cotton (std.dev.)
Iprodione	90 (± 9.4)	84 (± 4.0)
Pirimicarb	100 (± 1.2)	100 (± 1.4)

[a]Mean of two runs. Percent is based on analysis of pesticide only pipetted into an Erlenmyer (without a fabric specimen) taken as 100%.

lost to the air in the fumehood (the fan was left on during the 24 hour drying period). Both cotton and polyester/cotton fabrics were contaminated with pirimicarb. Control specimens were left in the fumehood with air movement for 1 day and 22 days after contamination. Specimens were also placed in Erlenmyer flasks, contaminated with pirimicarb, then closed with Teflon-lined screw caps. Those specimens, therefore, had no air movement for 1 day and 22 days after contamination. The percent pirimicarb residue remaining on these fabrics is listed in Table 4.

After contamination and air drying for 24 hours, the pirimicarb residue in cotton and polyester/cotton control specimens decreased to 68% and 69%, respectively, whereas the residue in "spiked-in-Erlenmyer" cotton and polyester/cotton specimens was 99% and 100%. After 22 days, 50% and 48% residues were found in cotton and polyester/cotton controls which were air dried; however, the percent residue remaining in "spiked-in-Erlenmyer" specimens remained essentially the same, that is almost 100%. Therefore, the pirimicarb residue in specimens is removed by the circulating air in the fumehood rather than chemical degradation, since the residue in specimens which were dried in closed Erlenmyer flasks did not decrease. This finding implies that pirimicarb residues in work clothing may "dust off" as the applicator works in the greenhouse. Hence, the workers, the worksite, and equipment could be directly and/or indirectly contaminated. In addition

Table 4

Pirimicarb Dispersion Experiment

Specimen	One Day		Twenty-two Days	
Ticle (n =1)	mg	%	mg	%
P[a]	0.1253	/	/	/
C-C[b]	0.0839	68	0.0631	50
C-SE[c]	0.1254	99	[illegible]	100
PC-C[d]	0.0868	69	0.0600	48
PC-SE[e]	0.1262	100	0.1239	98

[a]P = "pesticide only", without fabrics in Erlenmyer flask.

[b]C-C = Cotton control specimen, air dried in the fumehood.

[c]C-SE = Cotton "spiked-in-Erlenmyer" specimen.

[d]PC-C = Polyester/cotton control specimens, air dried in the fumehood.

[e]PC-SE = Polyester/cotton "spiked-in-Erlenmyer" specimen.

to dermal exposure to pirimicarb, greenhouse workers may inhale the pirimicarb residue that dusts off their work clothing. Respiratory protection for greenhouse workers becomes essential as they work in a confined space with less mixing of fresh air than out-of-door workers.

Residue Remaining After Laundering

The mean (in milligrams) residue remaining in fabrics after laundering with three different pre-laundering conditions is given in Table 5 for iprodione and Table 6 for pirimicarb and is summerized in Figure 1. The percent of iprodione residue remaining in specimens ranged from non-detectable to 0.9%, while a non-detectable amount to 0.7% pirimicarb residue remained in specimens after laundering. Less than 1% pesticide residues remain in the fabrics, regardless of the pre-laundering conditions, therefore, both pesticides can be successfully decontaminated by laundering.

Results of the ANOVA using original data are summerized in Table 7. The Kolmogorov-Smirnov Goodness of Fit Test (Table 8), however, indicated that the data were not normally distributed, and the Levene Test (Table 9) indicated that the data did not have homogeneity of variance. The assumptions of the ANOVA, that is, that all groups are normally distributed with equal variances, are therefore not met. This result is due to the fact that a large number of specimens had pesticide residues below the detection limit for the HPLC and therefore

Table 5

Mean Iprodione Residue Remaining in Unlaundered Controls and in Specimens after Laundering

Specimens	Cotton		Polyester/Cotton	
(n = 6)	mg (std. dev.)	% (std. dev.)	mg (std. dev.)	% (std.dev.)
UN[a]	0.2227 (± 0.021)	90 (± 7.7)	0.1976 (± 0.023)	80 (± 8.2)
None[b]	0.0013 (± 0.002)	0.5 (± 0.0)	0.0020 (± 0.002)	0.9 (± 0.0)
SW[c]	0.0008 (± 0.001)	0.4 (± 0.0)	ND[e]	ND
BW[d]	ND	ND	ND	ND

[a]UN = unlaundered control specimens. [b]None = Without pre-treatment/one wash.

[c]SW = Spray 'n Wash® pre-treatment/one wash.

[d]BW = Bleach pre-treatment/one wash.

[e]ND = Non Detectable. Below the detection limit of HPLC (3.5×10^{-6} mg per specimen).

Amount of Iprodione pipetted onto fabric: 0.2471 mg.

Table 6

Mean Pirimicarb Residue Remaining in Unlaundered Controls and in Specimens after Laundering

Specimens	Cotton		Polyester/cotton	
(n = 6)	mg (std. dev.)	% (std. dev.)	mg (std. dev.)	% (std.dev.)
UN[a]	0.0854 (± 0.002)	68 (± 1.6)	0.0879 (± 0.004)	70(± 2.8)
None[b]	0.0006 (± 0.000)	0.7 (± 0.0)	ND	0.04 (± 0.0)
SW[c]	0.0003 (± 0.000)	0.4 (± 0.0)	ND[e]	ND
BW[d]	ND	0.1 (± 0.0)	ND	ND

[a]UN = unlaundered control specimens.

[b]None = Without pre-treatment/one wash.

[c]SW = Spray 'n Wash® pre-treatment/one wash.

[d]BW = Bleach pre-treatment/one wash.

[e]ND = Non Detectable. Below the detection limit of HPLC (5.5×10^{-7} mg per specimen).

Amount of pirimicarb pipetted onto fabrics: 0.1268 mg

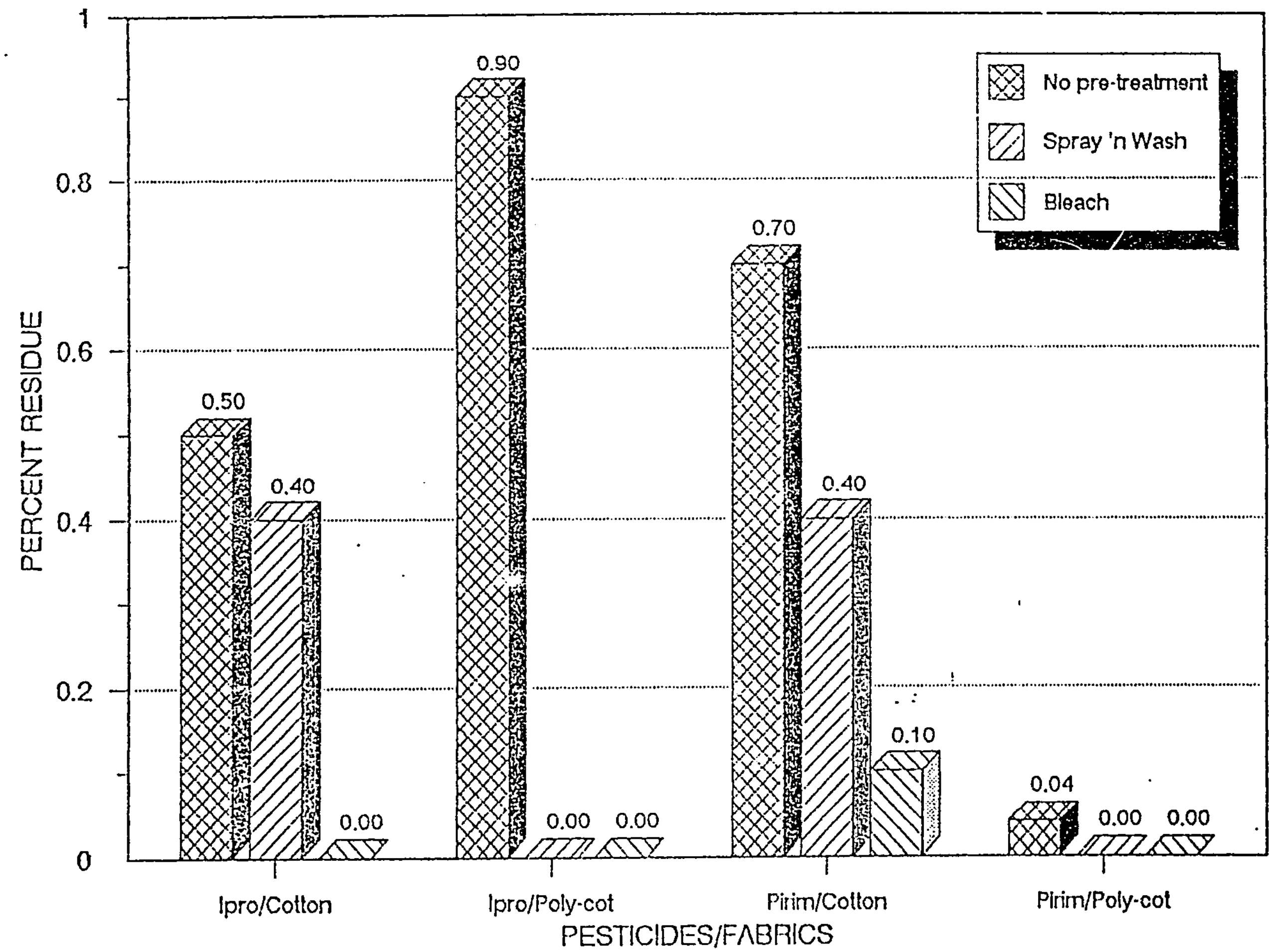

Figure 1. Mean percent Iprodione/pirimicarb residue remaining on cotton and polyester/cotton fabrics after laundering with or without pre-treatment

Table 7

Summary of ANOVA

Source of Variation	Sum of Squares	df	MS	F	P
Pest[a]	0.129	1	0.129	0.775	0.382
Fabrics[b]	0.660	1	0.660	3.969	0.051
Treat[c]	3.287	2	1.644	9.887	0.000 *
Pest by Fabrics	0.652	1	0.652	3.924	0.052
Pest by Treat	0.493	2	0.246	1.482	0.236
Fabrics by Treat	0.247	2	0.123	0.743	0.480
Pest by Fabrics by Treat	0.934	2	0.467	2.811	0.068

[a]Pest = type of pesticide;

[b]Fabrics = type of fabrics;

[c]Treat = type of pre-laudering conditions;

*significant at the 0.05 level.

Table 8

Summary of Kolmogorov-Smirnov Goodness of Fit Test

Most Extreme Differences			K-S Z	2-Tailed P
Absolute	Positive	Negative		
0.40376	0.40376	-0.30046	3.4022	0.0000 *

*significant at the 0.05 level, indicating distribution is not normal.

Table 9

<u>Summary of Levene Test</u>

Source of Variation	Sum of Squares	df	Mean Squares	F	P
Pest[a]	0.55	1	0.55	12.21	0.001*
Fabrics[b]	0.67	1	0.67	14.82	0.000*
Treat[c]	1.52	2	0.76	16.79	0.000*
Pest by Fabrics	0.00	1	0.00	0.00	0.990
Pest by Treat	1.01	2	0.51	11.21	0.000*
Fabrics by Treat	0.22	2	0.11	2.46	0.094
Pest by Fabrics by Treat	0.12	2	0.06	1.32	0.275

[a]Pest = type of pesticide;

[b]Fabrics = type of fabrics;

[c]Treat = type of pre-laundering conditions;

*non homogeneity of variance

a zero was used for those non-detectable findings in the analysis.

A nonparametric Robust Regression Analysis using rank data was therefore employed to analyze the results. The three independent factors were recoded into dummy variables. Ramsay's transformation was employed in a Conditional Nonlinear Regression (CNLR) procedure. A Robust regression model can be established from Table 10 as follows:

$$Y = 39.6626 + 3.3414\ B1 - 2.0316\ B2 + 9.6612\ B3 + 2.9805\ B4 - 9.8855\ B5 - 1.1600\ B6 + 2.9805\ B7 + 1.0535\ B8 - 1.5641\ B9 - 6.8005\ B10 - 1.5641\ B11$$

Where Y = pesticide residue in fabrics after laundering;

B1 = fabrics;

B2 = pesticides;

B3 = Spray 'n Wash® & bleach);

B4 = No pre-treatment & bleach);

B5 = fabrics x pesticides;

B6 = fabrics x B3;

B7 = fabrics x B4;

B8 = pesticides x B3;

B9 = pesticides x B4;

B10 = fabrics x pesticides x B3;

B11 = fabrics x pesticides x B4;

In the above statistical model, B3 (Spray 'n Wash® and bleach), B5 (interaction between fabrics and pesticides), and

Table 10

Summary of Robust Regression Analysis

Parameter	Label	Estimate	Lower 95% C. I.[a]	Upper 95% C. I.
B0[b]	constant	39.6626	36.0155	43.3097*
B1	fabric	3.3414	-0.3057	6.9886
B2	pesticide	-2.0316	-5.6787	1.6156
B3	Spray & bleach	9.6612	6.1071	13.2152*
B4	none & bleach	2.9805	-0.4180	6.3790
B5	fabric x pesticide	-9.8855	-13.5327	-6.2384*
B6	fabric x B3	-1.1600	-4.7141	2.3940
B7	fabric x B4	2.9805	-0.4180	6.3790
B8	pesticide x B3	1.0535	-2.5006	4.6075
B9	pesticide x B4	-1.5641	-4.9626	1.8344
B10	fabric x pesticide x B3	-6.8005	-10.3545	-3.2465*
B11	fabric x pesticide x B4	-1.5641	-4.9626	1.8344

[a]C. I. = confidence interval; *significant parameters

Table 11

Summary of Duncan's Multiple Range Test

Rank Means	Group[1]	Gp11	Gp3	Gp5	Gp6	Gp12	Gp10	Gp9	Gp1	Gp2	Gp8	Gp7	Gp4
25.5	Gp11												
25.5	Gp3												
25.5	Gp5												
25.5	Gp6												
25.5	Gp12												
32.4	Gp10												
32.8	Gp9												
33.5	Gp1												
33.6	Gp2												
48.4	Gp8	*	*	*	*	*							
58.9	Gp7	*	*	*	*	*	*	*	*	*			
60.2	Gp4	*	*	*	*	*	*	*	*	*			

[1]See Table 1 for description of groups. *significant differences at the 0.05 level.

B10 (three-way interaction among fabrics, pesticides, and pre-treatments) are significant parameters affecting residue removal as indicated in Table 10. Duncan's Multiple Range post hoc test was run to further reveal differences among 12 different groups (see Table 11). This analysis was carried out using rank data and Ramsay's Function to provide the weights. From Table 11, Group 8 (pirimicarb, cotton, Spray 'n Wash®) is significantly different from Groups 3, 5, 6, 11, and 12. Group 4 (iprodione, polyester/cotton, and no pre-treatment) and Group 7 (pirimicarb, cotton, and no pre-treatment) are significantly different from Groups 1, 2, 3, 5, 6, 9, 10, 11, and 12.

Test of Null Hypotheses

Null Hypothesis 1: There will be no significant interactions among the three independent variables, type of pesticide, fabric, and pre-laundering conditions.

It can be seen from Table 10 (parameter B10) that there is a significant three-way interaction (fabrics by pesticides by pre-treatments). Hence, null hypothesis 1 is rejected.

The significant interactions indicate , for example, that the effect of laundering pre-treatment depends on both fabric and pesticide, as described in the following section of null hypothesis 4. The mechanisms for the removal of pesticide residue by laundering from the textile fabrics are complex because of the many factors involved: type of pesticide, fabric, and pre-laundering conditions, as well as interactions among them. The laundering process also includes complex interactions of thermal, chemical, and mechanical energies from wash water temperature, detergents, auxiliaries, water minerals, agitation, etc. The effectiveness of residue removal is not dependent on a single factor, but a combination of factors. The three independent variables, type of pesticide, fabric, and pre-treatment, operate together to influence the percent residue removed.

Null Hypothesis 2: There will be no significant difference between iprodione and pirimicarb in percent residue remaining after laundering.

There is no significant difference between iprodione and pirimicarb in percent residue remaining after laundering (parameter B2 in Table 10). Therefore, null hypothesis 2 is accepted.

Pesticide chemical classification influences residue removal by laundering. Compared to other pesticide classes, such as organophosphates and organochlorines, the carbamate insecticides have been found to be more readily removed by laundering (Chiao-Cheng, 1984). The insecticide pirimicarb, which is a carbamate compound, was found in this study to be readily removed by laundering, confirming the results of

Chiao-Cheng (1984). The fungicide iprodione is a carboxamide and it was just as readily removed by laundering as the pirimicarb. This may be due to the complex combined effects of pesticides, fabrics, pre-laundering conditions, or may be the result of other laundering factors not verified in this study.

Pesticide solubility in water is one important indicator of the ease of residue removal by the aqueous laundering process. Because the herbicide glyphosate is very soluble in water, it is readily removed, even with cold water (50°C) (Samuel and Guillot, 1992); however, predictions on the ease of residue removal based only on water solubility are problematic. For example, 2,4-D ester has high water solubility, but it is still difficult to remove by aqueous laundering. Pirimicarb has a higher water solubility (2.7 g/L at 25°C) than iprodione (13 mg/L at 20°C); therefore, pirimicarb would be expected to be removed more easily by the aqueous laundering process than iprodione. In this study, however, there was no significant difference in percent pirimicarb and iprodione residue remaining after laundering. There was a sufficient volume of water used in the laundering process to dissolve both iprodione and pirimicarb residue on the fabric swatches (about 0.2 mg iprodione and 0.09 mg pirimicarb). Factors other than solubility may also influence residue removal. For example, Kim and Wang (1992) reported that high wash water temperature may increase the pesticide water solubility. The wash and rinse temperature (50°C and 40°C respectively) may have increased the water solubility of iprodione and pirimicarb and enhanced their removal.

Pesticide formulation is another important factor in residue removal. Previous studies found that wettable powder formulations are easier to remove by laundering than encapsulated and emulsifiable concentrate formulations. Because the powder has been treated to make it wettable, water readily wets out the powder on the fabric, and water and detergent begin to facilitate removal. The pirimicarb and iprodione used in this study are both in wettable powder formulation. The loss of pirimicarb from the unlaundered control specimens air dried in the fumehood indicates that much of this pesticide remains on the surface of the fabrics and is easily removed by air circulation. The agitation during laundering could mechanically remove some of the powder and this would did in the removal of pirimicarb by aqueous laundering.

Null Hypothesis 3: There will be no significant difference between 100% cotton and 65/35 polyester/cotton in percent residue remaining after laundering.

There is no significant difference in percent residue remaining after laundering between 100% cotton and 65/35 polyester/cotton (parameter B1 in Table 10); hence, null hypothesis 3 is accepted. This is perhaps partly due to the fact that the two fabrics are very similar in fabric characterization. There are variations in spaces between individual fibers and yarns of the two fabrics. The spaces determine the contact between the internal surfaces of fabrics and the pesticide particles. The two fabrics are fairly tightly woven, which may, to some extent, prevent pesticide particles from reaching the interior surface, thus they remain on the surface, making it easier to remove the pesticide residues by aqueous laundering.

Null Hypothesis 4: There will be no significant differences in percent residue remaining after laundering among no pre-treatment, Spray 'n Wash® pre-treatment, and chlorine bleach pre-treatment.

Null hypothesis 4 is rejected because the Duncan's Multiple Range Test shows that there are significant differences in percent residue remaining among the three different pre-laundering conditions, but that these differences are affected by interactions with both fabric and pesticide. The statistically significant differences are as follows:

(1) Spray 'n Wash® removes more iprodione residues than no pre-treatment from polyester/cotton, but not from cotton.

(2) In removal of pirimicarb, Spray 'n Wash® is not

statistically different from no pre-treatment for either fabric. There is, however, a significant difference between its effects on the two fabrics.

(3) Bleach removes more iprodione residues than no pre-treatment from polyester/cotton, but not from cotton; bleach removes more pirimicarb than no pre-treatment from cotton, but not from polyester/cotton.

(4) For each fabric/pesticide combination, there is no significant difference between Spray 'n Wash® and bleach pre-treatment.

Spray 'n Wash® is a prewash stain remover which contains a solvent and surfactant. The solvent can penetrate into fibers, especially the synthetic fibers, and dissolve grease and oil stains; surfactants disperse and solubilize the solvent/grease mixture in the wash water. This mechanism appears to help remove the iprodione and pirimicarb residues from both fabrics, but especially from the polyester/cotton fabrics.

Chlorine bleach is a popular laundry aid. The active component in the bleach solution is controlled by the equilibrium at different pH values.

$$(1)\quad NaOCl \rightleftharpoons Na^+ + OCl^-$$

$$(2)\quad HOCl \rightleftharpoons H^+ + OCl^-$$

$$(3)\quad HOCl + H^+ + Cl^- \rightleftharpoons Cl_2 + H_2O$$

In alkaline solution (pH > 8.5), reaction (1) predominates, while between pH 5 and pH 8.5, reaction (2) is significant. In acid solution (pH < 5), chlorine is present in the elemental form as shown in reaction (3) (Nevell, 1986). The pH value for Javex® chlorine bleach soaking solution at 50°C is 8.9, while the pH is 8.85 at 42°C (Perkins, 1992). The bleach solution is alkaline with OH^- and Na^+ ions, therefore, reaction (1) predominates. Iprodione reacts with OH^- and Na^+, forming a salt which is water soluble and can be removed from the fabrics by laundering (Belafdal, Bergon, & Calmon, 1986). Pirimicarb also reacts with OH^-, and is degraded into smaller compounds which are easier to remove by laundering. Possible reactions are shown in Figure 2 for iprodione and Figure 3 for pirimicarb.

Perkins et al. (1992) estimated that it would cost $1.25 per coverall per wash to use Spray 'n Wash® and $0.13 to use the Javex® chlorine bleach soak pre-treatment. Hence, the cost of Spray 'n Wash® may be prohibitive to the greenhouse operators and the extra time, effort and water required for the bleach pre-treatment may be problematic. The chlorine bleach pre-treatment also causes some loss of color and breaking strength of the protective clothing, which would add to the cost of work clothing as they would have to be replaced more frequently (Perkins, Rigakis, Crown, Armour, and Kerr, 1993). Since iprodione and pirimicarb residues are less than 1%, practically speaking, a single wash without pre-treatment can be considered an effective laundering procedure for these two pesticides. On the other hand, pirimicarb is a highly toxic insecticide. Although after one wash cycle, less than 1% pirimicarb residue remains on fabrics, over a long period the residue concentration may build up. The insecticide bioactivity of this residue is still unknown. The long term accumulation effects of highly toxic insecticide residues may cause health problems. Therefore, pesticide applicators may still wish to periodically use Spray 'n Wash® or chlorine bleach as a pre-treatment in removal of pirimicarb residues on contaminated work clothing, especially under certain circumstances such as an accidental over-contamination with pirimicarb.

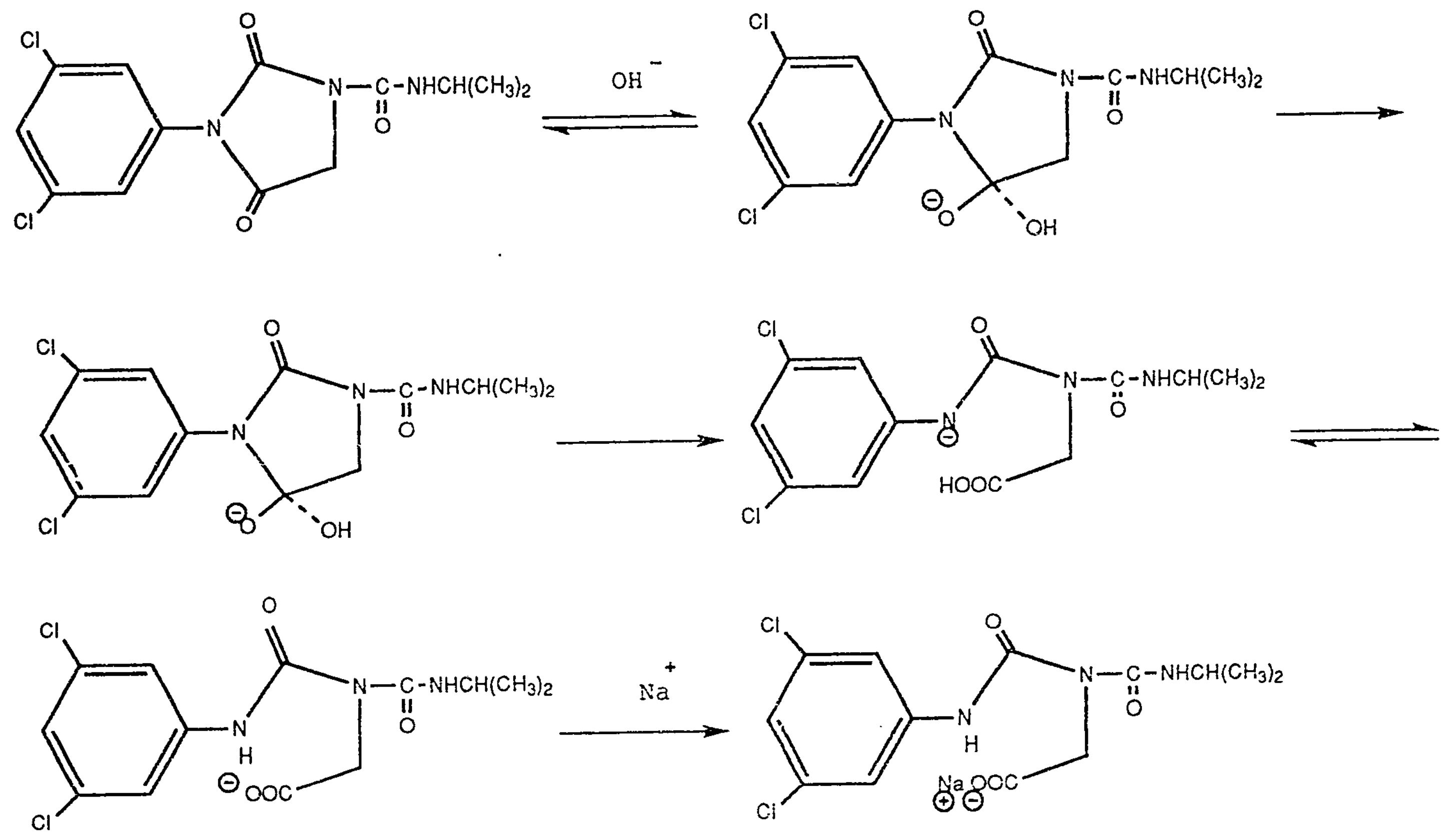

Figure 2. Proposed Mechanism for Bleach Degradation of Iprodione

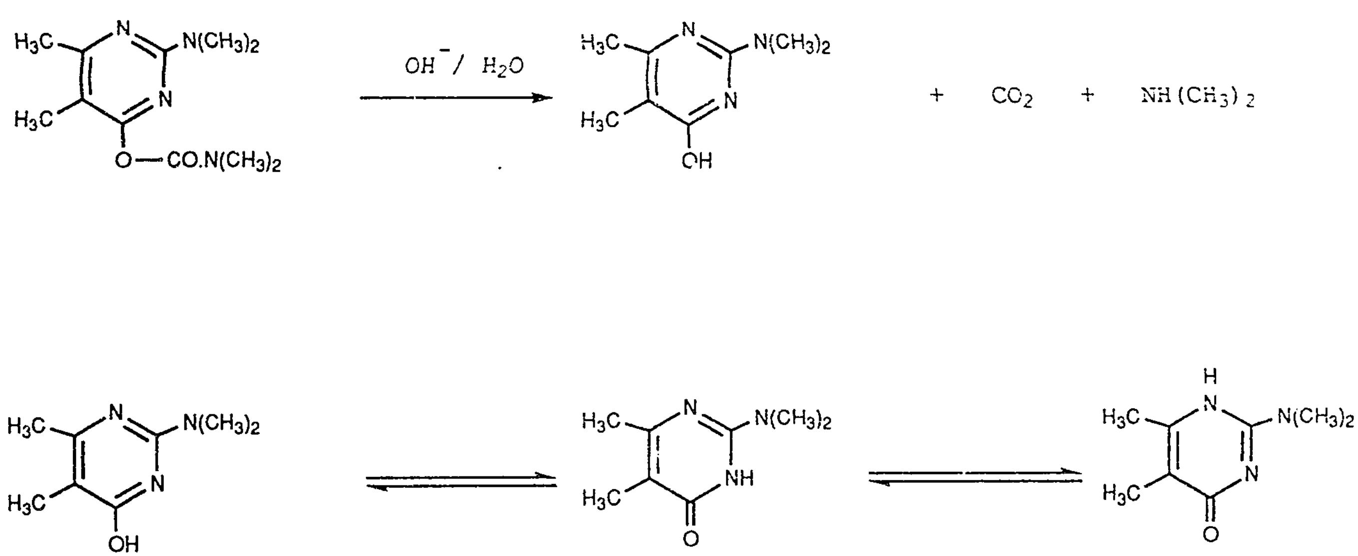

Figure 3. Proposed Product of Bleach Degradation of Pirimicarb

CHAPTER 5 SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

In this chapter, the study is summarized and some conclusions are drawn based on the experimental results and statistical analysis. Some recommendations are also made for Alberta greenhouse pesticide applicators and further research.

Summary

The overall purpose of this study was to contribute to the development of effective laundering procedures for decontamination of clothing soiled with pesticides. Two pesticides, the fungicide iprodione and the insecticide pirimicarb, were used. They represent different chemical classes, carboxamide and carbamate, respectively. They were chosen because they are widely used in Alberta greenhouses. In addition, no laundering decontamination studies have been found to date on work clothing contaminated with either iprodione or pirimicarb. Two fabrics, 100% cotton and 65/35 polyester/cotton, were chosen for this study. They are representative of fabrics commonly found in protective clothing worn by pesticide applicators, and have been previously used by researchers in pesticide decontamination studies. The two fabrics were analyzed to determine fabric mass, thickness, threads per unit length and weave. Two laundering pre-treatments were selected in order to determine their influences on the ease of removal of iprodione or pirimicarb from the two fabrics. Spray 'n Wash® has been found to be effective in removing residues of pesticides from different chemical classes (Nelson et al., 1992), and a bleach pre-treatment has been found very effective for the removal of the organochlorine insecticide chlorpyrifos (Perkins et al., 1992).

The contamination, laundering pre-treatments, and laundering procedures outlined by Perkins et al. (1992) were followed. The extraction solvent and evaporation procedure for iprodione- and pirimicarb-contaminated specimens were based on preliminary experiments and previous research. The residue remaining in both laundered and unlaundered specimens contaminated with pesticides was determined by HPLC. Based on the research work of Cabras et al. (1983), the HPLC conditions for the chromatography of iprodione and pirimicarb were modified, developed and optimized.

For the data collected, statistical analysis was performed employing SPSS® software and using a nonparametric Robust regression analysis technique to test the null hypotheses. Conclusions are based on the statistical analysis.

There was no significant difference in percent iprodione and pirimicarb residues remaining after laundering on the cotton and polyester/cotton fabrics. Spray 'n Wash® or chlorine bleach pre-treatment was effective in removal of iprodione residues from polyester/cotton fabrics; bleach pre-treatment was also effective in removal of pirimicarb residues from cotton fabrics. Regardless of the pre-treatment, less than 1% iprodione or pirimicarb residue remained on fabrics. Becuase pirimicarb is a highly toxic insecticide, pesticide applicators may consider periodically using Spray 'n Wash® or chlorine bleach as a laundering pre-treatment in removal of pirimicarb residues from contaminated work clothing.

It appears that pirimicarb remains on the surface of cotton or polyester/cotton fabrics rather than penetrating deeply into the fibers and as a liquid spill dries, the pesticide can "dust off" in the air. After 22 days of exposure to air circulation, only about 50% of the applied pirimicarb is found on cotton or polyester/cotton fabrics. Research showed that this decrease was not caused by breakdown of the pesticide.

Conclusions

The fungicide iprodione and the insecticide pirimicarb are widely used in Alberta greenhouses. The greenhouse workers face potential health problems if their work clothing contaminated with iprodione or pirimicarb is not properly decontaminated before re-use.

Work clothing soiled with diluted iprodione or pirimicarb can be effectively decontaminated through laundering, using a warm wash (50°C) for 12 minutes, followed by two cool rinses (40°C). After one wash cycle, 65/35 polyester/cotton specimens contaminated with iprodione or 100% cotton specimen contaminated with pirimicarb have the highest percent residue remaining after laundering (0.9% and 0.7%, respectively). Laundering pre-treatments such as Spray 'n Wash® or Javex® chlorine bleach soak pre-treatment effectively reduce iprodione and pirimicarb residues remaining in fabrics after laundering. Less than 1% iprodione or pirimicarb residue remains in fabrics after a single wash cycle without pre-treatment, or after one wash cycle with either Spray 'n Wash® or bleach pre-treatment.

The possible mechanisms for the removal of the two pesticides are the following. Much of wettable powder pesticides remains on the surface of fabrics and thus they are readily removed by agitation during laundering process. The water solubility of each pesticide may be increased during warm wash procedures. In addition, it has also been found that the factors of pesticide, fabric, and pre-treatment interact to influence pesticide residue removal by aqueous laundering, suggesting that the decontamination process is complex involving mechanical, chemical, and thermal factors. The ease of removal of the residues and possible mechanisms suggested apply to the specific dilutions and formulations of the pesticides used in this study. This finding also supports previous studies on removing wettable powder pesticide residues from fabrics by laundering. There are implications that other wettable powder pesticides may be readily removed by aqueous laundering.

It was noted that only about 50% of the applied pirimicarb remained on cotton or polyester/cotton fabrics after they had been exposed to air circulation for 22 days. This finding implies that much of the pirimicarb residues are on the surface of fabrics and disperse into the air once the contaminated fabric has dried. This may cause direct and/or indirect contamination to the greenhouse workers, the work environment, and the equipment. Respiratory protection for greenhouse workers is important to minimize pirimicarb inhalation risks.

Recommendations

Some recommendations for Alberta greenhouse pesticide applicators are as follows.

1. Use a warm wash (50°C) for 12 minutes, followed by two rinses (40°C) to remove iprodione or pirimicarb residues from contaminated work clothing.

2. Consider the periodic use of Spray 'n Wash® or chlorine bleach as a laundering pre-treatment in removal of pirimicarb residues from contaminated work clothing.

3. Use respiratory protection equipments when dealing with pirimicarb.

Some suggestions for further study are as follows:

1. Other pesticides which are widely used in Alberta greenhouses but have not been studied, for example,

dienochlor, diquat, fenbutatin oxide, picloram, and terrazole, should be investigated to determine the effectiveness of decontamination procedures.

2. Other pesticides which are used by Alberta commercial applicators or in agriculture, and are difficult to decontaminate, for example, 2,4-D ester, should be investigated to determine the effectiveness of residue removal by laundering.

3. If the pesticides to be studied come in various formulations, all formulations should be studied. In addition, research should include the dilution normally used and the concentrate if liquid formulations are made.

4. Qualitative analytical methods, SEM (Scanning Electron Microscopy) or a bioassay test, may be employed to evaluate pesticide distribution in the fabrics or the biological activity of the residues remaining in fabrics after laundering, if a very toxic pesticide is under study.

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APPENDIX A-1 PESTICIDES MOST COMMONLY USED IN ALBERTA

Pesticide	Category	Users
Aldicarb	Insecticide	Greenhouse
Avadex BW	Herbicide	
Captan	Fungicide	Greenhouse
2,4-D	Herbicide	Aerial,Landscape Industrial,Agriculture
Diazinon	Insecticide	Greenhouse,Structural Landscape
Dienochlor	Acaricide	Greenhouse
Diquat	Herbicide	Industrial
Endosulphan	Insecticide	Greenhouse
Fenbutatin Oxide	Insecticide	Greenhouse
Iprodione	Fungicide	Greenhouse
Malathion	Insecticide	Structural,Aerial Landscape,Greenhouse
Parathion	Insecticide	
Permethrin	Insecticide	Structural,Landscape Greenhouse
Picloram	Herbicide	Aerial,Industrial
Pirimicarb	Insecticide	Greenhouse
Terrazole	Fungicide	

Source: Crown, E., & Armour, M. A. (1991). Effective decontamination procedures for clothing, equipment and spills. Alberta Occupational Health and safety Heritage Grant Program.

APPENDIX A-2 THE OPTIMAL HPLC CONDITIONS FOR IPRODIONE OR PIRIMICARB

The optimal HPLC conditions for iprodione are:

Flow rate: 0.3 mL/min.

Pressure: 1300 psi

Detection wavelength: 212 nm

Mobile Phase: 80:20 (acetonitrile:double distilled water)

Threshold: 3

Attenuation: 5 (for unlaundered sample solution)

3 (for laundered sample solution)

Peak width: 0.20

The optimal HPLC conditions for pirimicarb are:

Flow rate: 0.5 mL/min.

Pressure: 3500 psi

Detection wavelength: 245 nm

Mobile phase: 50:50 (buffer solution:acetonitrile)

Threshold: 0

Attenuation: 5 (for unlaundered sample solution)

3 (for laundered sample solution)

Peak width: 0.20

APPENDIX A-3 INTERPRETATION OF HPLC GRAPHS

This is an example of how to interpret an HPLC graph. The sample in Figure 2 is "pirimicarb only". The quantity 0.5 mL of 0.5 mg/mL pirimicarb (50.7% active ingredient) was spiked into an Erlenmyer in which there was no fabric specimen.

A calibration formula for the HPLC was obtained beforehand as follows:

$Y = 882.55\ X - 0.0035$

Where X = pesticide residue remaining before multiplication by the dilution factor;

Y = peak area ($\times 10^{-6}$).

The retention time for pirimicarb in this HPLC graph is 3.380 min. Hence, the peak area of pirimicarb residue at 3.380 min is 1.110106 ($\times 10^{-6}$).

So, $X = (Y + 0.0035) / 882.55 = 1.262 \times 10^{-3}$

The sample solution had been diluted 100 times. Hence, with this dilution factor, the pirimicarb residue is

$1.262 \times 10^{-3} \times 100 = 1.262$ (mg)

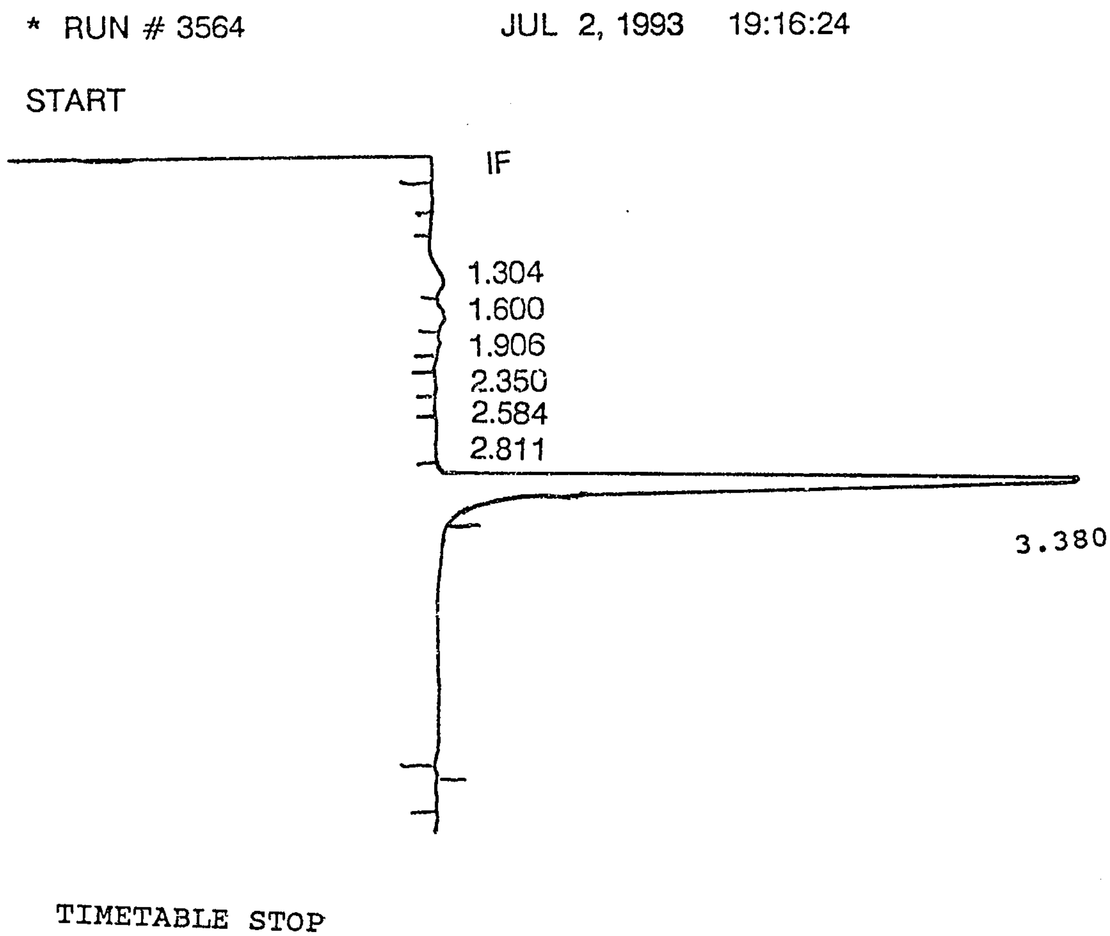

Figure 4. HPLC Graph of Pirimicarb Residue

RUN # 3564 JUL 2, 1993 19:16:24

RT	AREA	TYPE	WIDTH	AREA%
1.304	40401	VV	.252	3.26262
1.600	27843	VV	.251	2.24848
1.906	20590	VV	.150	1.66276
2.350	10378	VV	.147	.83808
2.584	11712	VV	.147	1.39473
3.380	1110106	PB	.168	89.64752

TOTAL AREA=1238301
MUL FACTOR=1.0000E+00