To the Graduate Council:

I am submitting herewith a thesis written by Unchin Cho entitled "Barrier Efficiency of Polyolefin Nonwovens, Cotton Denim, and Cotton Knit Protective Apparel Against Pesticides". I have examined the final copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Human Ecology.

Maureen Dever

Maureen Dever, Major Professor

We have read this thesis
and recommend its acceptance:

Nancy Fair

Thomas Mueller

Accepted for the Council:

Carolyn Winkler

Associate Vice Chancellor
and Dean of The Graduate School

BARRIER EFFICIENCY OF POLYOLEFIN NONWOVENS, COTTON DENIM, AND COTTON KNIT PROTECTIVE APPAREL AGAINST PESTICIDES

A Thesis

Presented for the

Master of Science

Degree

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Unchin Cho

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DEDICATION

This thesis is dedicated to my parents

Mr. Chunggil Cho

(다정한 아빠)

and

Ms. Kumsun Yu

(사랑하는 엄마께)

who have inspired me to pursue my education.

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ABSTRACT

Two test methods were used to determine pesticide penetration depending on different types of protective clothing material; one was a spray test and the other was a weight (pressure) test. A laboratory spray chamber was used to spray pesticides (Leonas, 1988). The laboratory spray system simulates field studies by facilitating of the droplet size and amount of pesticide delivered to the fabric. For the weight test, a 2 psi weight for one minute was used to simulate elbow or forearm pressure after spray test. Four commercial nonwovens, one knit, and one woven materials were selected based on their different fiber characteristics and because the fabrics represented what workers typically wear. Spunbond-meltblown-spunbond (SMS), microporous film laminated spunbond (MSB), nonporous film coated spunbond (CSB), and Tyvek®1422 are provided by Kappler Protective Apparel & Fabrics and 100 % t-shirt cotton knit and 100 % cotton denim woven were provided by Test Fabrics, Inc., Middlesex, NJ. Two pesticides were selected because they represent the most commonly used commercial and residential applications; atrazine (herbicide) and chlorpyrifos (insecticide) respectively. According to the recommendation of agricultural scientists, 2.5 % (v/v) concentration active ingredient of atrazine (Atrazine 4L®) and 1.0 % (v/v) concentration active ingredient of chlorpyrifos (Dursban®), as general concentrations in actual field applications, were selected. A multi-layer sample consisted of 3 layers; a protective apparel fabric, a cotton knit collector and a mylar backing, was prepared similar to that used in study by Leonas (1985) and Dimit (1989). The cotton knit was to simulate the garments of agricultural workers, and the mylar prevent pesticide penetration from back side during the spray. The pesticide was extracted from the cotton and was analyzed quantitatively using a Gas Chromatography (GC) and a High Performance Liquid Chromatography (HPLC). MSB, CSB and Tyvek®1422 showed good barrier efficiency against atrazine and chlorpyrifos. MSB and CSB had excellent barrier efficiency against both atrazine and chlorpyrifos while Tyvek®1422 had an excellent efficiency against atrazine. SMS nonwoven showed the worst protection among those nonwovens although it provided good protection against atrazine. MSB would be a good choice for protective clothing material in case of hot and humid outside weather, because micropores in outer polyolefin film layer could allow the evaporation of the water vapors more effectively than CSB and Tyvek®1422. CSB (about half price of MSB) and Tyvek®1422 are cost effective. Blue denim provided good protection against atrazine while it did not against chlorpyrifos. Cotton provided the worst protection against the both atrazine and chlorpyrifos whether weight was

applied or not while protection of blue denim was decreased almost twofold when weight was applied.

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CHAPTER I

INTRODUCTION

1.1 PESTICIDE HAZARDS

Crop protection chemicals (pesticides) protect us from insects, weeds, disease and hunger, but exposure to some pose a risk of cancer, birth defects, genetic mutation, and sterility (Boraiko, 1980). Short-term symptoms resulting from pesticide exposure include nausea, eye and skin irritation, headaches, and insomnia (Kahn, 1976). Long-term symptoms of chronic organophosphate exposure were difficulties in focusing attention and maintaining alertness (Smith et al., 1968). Savage et al. (1988) suggests that chronic neurological problems may follow acute organophosphate poisonings. Cancer may be another long-term effect of pesticide risk (Leavitt et al., 1988). The majority of occupational poisonings are dermal in nature. Dermal exposure to pesticides accounts for 87-90% (Wolfe et al., 1972) and less than 1% of total exposure is via respiration. The importance of pesticide dermal exposure has not received sufficient attention because the oldest pesticides are absorbed through the skin to a lower concentration than the pesticides used currently (Matsumura et al., 1980). Toxicity is the inherent capacity of a compound to be poisonous at some level. Toxicity is expressed as a quantity of the substance as compared to the weight of the animal. There is an amount (a threshold) for toxic response, and any amount below that level is harmless. The LD_{50} value is the statistically estimated dosage fatal to 50% of a large population applying to oral and dermal dosages. The LD_{50}s are expressed as milligrams of toxicant per kilogram of body weight, the dose that kills 50 percent of the test animals, which are usually laboratory rats. Substances are graded according to their acute toxicity to animals, as follows (Foraberg et al., 1986):

Level	Median Lethal Dose (LD_{50}), Dermal Rat or Rabbit, mg/kg
Very high acute toxicity	<50
High acute toxicity	50 to 400
Medium-to-moderate acute toxicity	400 to 2000
Low acute toxicity	.....

However, hazard (degree of danger) is linked to exposure and toxicity; i.e., it is the chance that the material will or will not elicit a negative response. If someone is not exposed, there is no hazard. If someone is exposed to trace amounts, the chances are that there is still no hazard.

1.2 NONWOVEN MARKETS RESEARCH

In 1996, 2.0 million metric tons (almost 4.5 billion pounds) of nonwoven fabrics were purchased worldwide (Shariq et al., 1997). Disposable items such as diapers, medical gowns and filters, are used one or more times and then thrown away, while durable goods such as geotextiles, interlinings and roofing last throughout the lifetime of the application. In the U.S. more than half of the disposable nonwovens bought ($4 billion market) are diapers and incontinence and feminine hygiene products, where spunbonds are predominant (Wuagneux, 1997).

1.3 PROTECTIVE APPAREL NONWOVENS RESEARCH

Other disposable nonwovens such as wipes and rolls, fabric softeners, oil sorbents and protective apparel have been increased in volume to develop and tailor individual products (Shariq et al., 1997). Spunbonded, melt blown and SMS nonwovens play an important role in medical apparel and surgical pack items, such as drapes, gowns, mask media, mask facings and head and shoe coverings ($1 billion business in 1997) as disposable end use (Wuagneux, 1997). Spunbonded and SMS material also play a significant role in protective apparel and use a market that is valued at approximately $90 million in North America (Wuagneux, 1997).

1.4 PURPOSE OF STUDY

The purpose of this study was to evaluate the effectiveness of selected fabrics in terms of pesticide penetration. Also, the research evaluated pesticide penetration of the selected fabrics when 2 psi pressure was applied to the contaminated samples in terms of pesticide penetration.

OBJECTIVES

The specific objectives of the research were:

1. To investigate the differences in selected fabrics in terms of pesticide penetration.
2. To investigate the difference in selected fabrics in terms of pesticide penetration when the two psi pressure was applied to the pesticide contaminate fabrics.
3. To investigate the difference between two pesticides of different classes in relation to pesticide penetration through the selected fabrics.
4. To evaluate whether fabric construction is related to the pesticide penetration.
5. To determine if fiber content has an effect on pesticide penetration.

HYPOTHESES

The research investigated whether the independent variable of type of fabric revealed difference in penetration. In addition, the research investigated which fabric type provided the best barrier to pesticide penetration. The null hypotheses are stated below:

1. There is no significant difference in pesticide penetration of selected fabrics.
2. There is no significant difference in pesticide penetration of selected fabrics when 2 psi pressure is applied.
3. There is no significant difference in two pesticides, namely atrazine and chlorpyrifos.
4. There is no significant difference in finish in pesticide penetration.
5. There is no significant difference in method of chemical analysis (GC, HPLC).

LIMITATIONS

The limitations of the research are stated below:

1. Only two pesticides were used in this study.
2. Only six fabrics were used in this study.
3. Only two psi weight was applied for one minute.
4. The study sponsored by Kappler Safety Group, was limited to one year from conception January 1997 until the final report that was due November 7 1997.

CHAPTER II

REVIEW OF LITERATURE

2.1 PROTECTIVE CLOTHING

Protective garments are designed to protect the wearer or the wearer's clothing from contamination by hazards as diverse as dirt, grease, or chemical biological radioactive hazardous substances, which can cause injury, longer term health problems, or death. There is no ideal protective clothing material, which can provide protection from all chemicals. The best way to select proper protective clothing is to test the hazardous chemical that would come in contact with the proposed material. The appropriate protective material can be selected with the knowledge of its breakthrough time. Limited use protective apparel is constructed of fabrics produced via any of several nonwoven processes, combinations of different nonwoven materials, or combinations of nonwoven fabrics and films. The fabric components are chosen for their unique ability to meet specific user performance requirements. These performance requirements are a balance between the right level of protection, comfort for the wearer, and the total cost of the garment. A significant portion of industrial protective apparel is used for dirty jobs, protecting the wearer from contact with dust or grease. The environmental restoration marker is another important market for sales of limited usage garment. Other large marker segments include asbestos/lead abatement and chemical handling in manufacturing and agriculture. The most important factors affecting the limited use of industrial protective clothing industries are government regulations and emphasis on worker health and safety. Growth in this industry has been driven primarily by government regulations starting with the 1970 passage of the Occupational Safety and Health Act, which established OSHA. Other significant government regulations impacting this industry are (Deeg et al., 1997):

- the Resource Conservation and Recovery Act (RCRA), which addressed the management of regulated hazardous waste, its storage and disposal
- the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA), known as the superfund act
- the Superfund Amendments and Reauthorization Act (SARA)

- the Asbestos Hazard Emergency Response Act (AHERA)
- OSHA's Rule for Occupational Exposure to Blood borne Pathogens
- the EPA's Worker Protection Standard for Agricultural Pesticides.

DuPont's Tyvek®, flash spun polyethylene nonwoven fabric, continues to dominate this industry (Deeg et al., 1997). SMS (spunbond/meltblown/spunbond) fabrics and laminates of film and nonwoven make up most of the rest of garment fabrics used. The development of microporous membrane materials has made better protection with comfort available to the user. Microporous membrane-based garment fabrics are expected continually the fastest growing garment fabric. Especially, characteristics of these fabrics are improved over the still relatively simple constructions used today and find applications in more and diverse markets (Deeg et al., 1997). In this market segment, Gore & Associates pioneered the use of "breathable" liquid chemical barrier garments with its Gore-Tex® fabrics. The leading U.S. manufacturers of industrial protective clothing include Kappler, Lakeland, Mar Mac, Kimberly Clark, with Kappler being the dominant and most sophisticated garment manufacturer. Kappler has developed a family of proprietary garment fabrics as well as the "CPF" line for chemical protective clothing and the "Pro-Shield" family for general protection applications (Deeg et al., 1997). Microporous membrane-based fabrics are expected to continue to replace more traditional fabrics and become widely used in most major markets where their unique balance between protection and comfort is valued. ASTM Committee F-23 on Protective Clothing was organized in 1977 by a group of concerned individuals representing both producers and users of protective clothing. F23's function is to develop voluntary standard test methods, terminology, classifications, and performance specifications for protective clothing used against hazards in the workplace. Specific test methods were needed to assess the performance of protective clothing to particulate and pesticides as well as human factors, such as heat stress, dexterity and sizing. The recent reorganization of F 23, composed of seven technical and five administrative subcommittees, has the responsibility for nine standard test methods on protective clothing (Henry, 1989). The Environmental Protection Agency (EPA) revised their Worker Protection Standard and issued a final rule that became effective October 20, 1992. This standard requires the use of personal protective equipment (PPE) for agricultural workers exposed to pesticides. Standards of F 23 are shown in Table 2.1.

Table 2.1 Environmental Protection Worker Protective Standard F23; Personal Protective Equipment for Agricultural workers Exposed to Pesticides

Test Method	Description
F739-85	Standard Test Method for Resistance of Protective Clothing Materials to Permeation by Liquids or Gases
F903-87	Standard Test Method for Resistance of Protective Clothing Materials to Penetration by Liquids
F955-85	Standard Test Method for Evaluation Heat Transfer Through Materials for Protective Clothing Upon contact with Molten Substances
F1001-86	Standard Guide for Selection of Chemicals to Evaluate Protective Clothing
F1002-86	New Standard Performance Specifications for Protective Clothing for Use by Workers Exposed to Specific Molten Substances and Related Thermal Hazards
F1052-87	New Standard Test Method for Thermal Protective Performance of Materials for Protective Clothing for Hot Surface Contact
F1154-88	New Standard Practice for Quantitatively Evaluating the Comfort Fit Function and Integrity of Chemical Protective Clothing Suit Ensembles
F1186-88	Classification System for Chemicals According to Functional Groups

2.1.1 Protective Clothing Materials

A majority of workers dealing with pesticides from five states said that they usually wore long-sleeved shirts and jeans or work pants when applying pesticides (Rucker et al., 1988). Such choices are consistent with generally accepted recommendations to cover arms and legs as well as the torso. A majority of the growers in each state also reported wearing gloves that were made of either 30-49 % waterproof vinyl or rubber or 20-48 % leather when applying pesticides. Leather or canvas gloves tend to absorb and retain pesticides and therefore, are not recommended. The most popular items for foot and head coverings were leather shoes and baseball caps respectively, which again potentially result in absorption and retention of pesticides (Protective Clothing for Pesticide Users, 1986). Few respondents wore waterproof jackets, pants or boots. Since coveralls made of spunbond olefin can withstand machine laundering up to four times (Laughlin and Roger, 1990), much research on the fabrics after laundering are needed.

2.1.2 Woven and Knit Materials

Fabrics that are commonly used for work clothing include cotton, polyester and their blends. These fabrics are used as protective clothing because of their comfort and washability (Laughlin et al. 1986). Chemical degradation (penetration) of cotton fabrics is related to the wetting and water or pesticide solution holding capacity. Thus, cotton twill and poplin, which had larger diameter yarns and more yarn exposure on the surface of the fabric than broadcloth, exhibited greater strength reduction. On the other hand, the ability of twill and poplin fabrics to hold and transport liquids were lesser extent compared to cotton broadcloth from one surface to the other (wicking). Smaller wicking ability than cotton broadcloth may enhance the dermal protection afforded by these fabrics (Raheel et al., 1985). In a study by Orlando et al. (1981), six fabrics were compared in terms of retention and penetration of pesticides. The fabrics were chambray (100 % cotton woven), chambray with a soil-release finish (100 % cotton woven), Tyvek®, Crowntex® (laminated with two plies of facial grade tissues), single ply polypropylene, and Gore-Tex® (nylon woven outer fabric laminated with PTFE film). The fabrics that were penetrated the greatest amount of pesticide were the two cotton chambray fabrics. The capillary action of the closely woven structure of the fabric combined with the low contact angle of cotton possibly explains the high level of penetration of pesticide. Obendorf and Solbrig (1986) conducted scanning electron microscopy of 50/50 polyester/cotton unfinished fabric contaminated with pesticide. Higher concentrations of malathion and methyl parathion were observed on the

surface and in the lumen of the cotton fibers of the fabric. Easely et al. (1981) observed the degree of contamination of methyl parathion on 100 % cotton fabric and 50/50 polyester/cotton fabrics. Durable press finishes on cotton/polyester fabrics increase the hydrophobic nature of the cotton fibers while decreasing the hydrophobic characteristics of the polyester fibers. Resin finished cotton formed intra-fiber cross-links, which reduce the hydrophilicity of cotton fabric because cellulose hydroxyl groups for interaction with water are less available (Raheel and Gitz, 1985). Laughlin et al. (1986) observed that durable press fabrics were more resistant to wetting by pesticide solutions than untreated fabrics because resin treated fabrics tended not to wick faster than untreated fabrics. Moisture transported along and between fibers and yarns rather than by absorbency into the internal fibers.

2.1.3 Nonwoven Materials

About 43 percent of the nonwoven process patents issued in 1996 involved combinations of two or more nonwoven technologies in achieving a new and novel process (Smith, 1997). This shows the increasing importance and power of combinations of technologies in achieving innovations in nonwoven processing.

Nonwoven Combination Process (Smith, 1997):

- Nonwoven plus films (apertured, microporous, multi-layered, etc.)
- Perforated film plus fiber
- SMS, SAMAS, SMMS, SMA, S/Film
- Spunbonded plus fiber plus spunlaced
- S/Pulp/S with waterjet entanglement and thermal bonding (bicomponent spunbond)
- SMS oxidative degraded surface filaments
- Equipment development and integration

"Sontara" spunlaced, "Tyvek" flash spun polyethylene, and "Typar" spunbonded polypropylene nonwovens are produced by DuPont, and "Kimguard" SMS, used in healthcare products, are manufactured by Kimberly-Clark.

2.1.3.1 SMS

Spunbonded, melt blown and SMS nonwovens have an important role in medical apparel and Surgical pack items, such as drapes, gowns, mask media, mask facings and head and shoe coverings ($1 billion business) as disposable end use (Wuagneux, 1997). Wuagneux (1997) said

that spunbonded and SMS material also play a significant role in protective apparel end uses a market that is valued at approximately $90 million in North America. Spun bonds, made of continuous filaments, are considered a unique class of materials within the general category of nonwovens. Four basic polymer types are used to manufacture spunbonded nonwovens: polypropylene, polyethylene, polyester and nylon. Spunbonds are distinguished from other nonwovens in their one-step manufacturing process. Most SMS nonwoven fabrics are made of polypropylene. Characterized by a larger surface area and small pore size, melt blown nonwovens differ from traditional spunbonds in their lower fiber denier or fineness as well as their use of discontinuous filaments. Meltblown fabrics, like most spunbonds, are manufactured directly from thermoplastic resins, with most commercial meltblown production using high melt polypropylene. Nonwoven fabrics made of polypropylene have the following characteristics (Salamie, 1987):

- High abrasion resistance
- Low specific gravity-high covering power
- Can be thermal bonded and thermoformed
- Processable on most conventional equipment
- High wickability
- Can be made into microdenier structure
- Can be made into smooth, soft structures
- Overall favorable price/performance properties

It is also cost effective that SMS composite fabrics are used in broad applications.

2.1.3.2 Tyvek®

Tyvek® consists of fine continuous interconnected polyethylene filament arranged in a thin web that can be thermally bonded to film, fabric, and paper. Because of its unmatched protective barrier property, Tyvek® is most advantageous for industrial protective apparel. There are many types of Tyvek® material: uncoated Tyvek® (1422A), polyethylene coated Tyvek®, Saranex® film laminated Tyvek® and so on. Saranex® coated Tyvek® provided a significantly higher resistance against Arochlor®1254 than polyethylene coated Tyvek®. In Schwope's research (1984), Saranex® laminated Tyvek® provided a better protection for cresol and o-toliduine than polyethylene coated Tyvek® with breakthrough times of 40 to 60 minutes for cresols and less than five minutes for o-toliduine. The breakthrough time was less than five minutes for toluene in both composites. On the other hand, Tyvek® showed the greater heat sensation and discomfort

compared to Gore-Tex® and cotton chambray (Orlando et al, 1981), yet the cost may be too great for disposable apparel.

2.1.3.3 Laminated or Coated Nonwovens

There are two film reinforcement categories of protective properties of films, monolithic and microporous (Brown, 1995). Porous film reinforcements allow the bulk flow of air through the pores, relying on filtration mechanisms against air-borne biohazards, and resist the penetration of challenging liquids. Monolithic (nonporous) film reinforcements do not allow the bulk flow of challenging air or challenging liquids. Monolithic (nonporous) film onto spunbond nonwoven has good barrier efficiency and is economical. This type of monolithic nonwoven fabric has ventilation problems. If the wearer is very active or naturally perspires heavily, condensation may be formed in the inner garment, which can cause discomfort, or more seriously, soak through to the insulation layers. Ventilation holes or flaps can provide some relief in highly susceptible areas such as the underarm and back, but they cannot cope with insensible perspiration produced over the rest of the body. New fabrics have appeared over the last 10 years, which satisfy in considerable measure the apparently conflicting requirements of a high degree of waterproofness and breathability. One successful example is the Gore-Tex® laminate which transmits perspiration through a PTFE film which is laminated between outer and inner materials, using a discontinuously applied adhesive (Lomax, 1984). Porous film reinforcements affect various characteristics of the challenging liquid. In Shaw's research (1992), fabrics laminated to PTFE membrane and treated with a water-repellent finish, showed considerable variation in the sorption of pesticide (diazinon) by fabric samples taken from different locations in the warp and filling directions. His another research (Shaw and Kenneth, 1991) showed a variation in the sorption rate of pesticide within the same treatment when chlorpyrifos was applied to the commercial fabric (polyester, laminated to PTFE membrane and treated with a water-repellent finish). This variation could be due to the inconsistency in the water-repellent finish on the fabric or to other processing problems. Back scattered electron imaging (BEI) showed that malathion, an organophosphate, was retained by all three layers (woven and two microporous membrane layers) of a three layer GoreTex® fabric. The pesticide also penetrated through the membrane to the back fabric (Shaw, 1993). The penetration of diazinon to the back of the fabrics, GoreTex® fabric with finer yarns (polyolefin) showed less penetration than polyester and acrylic, which had coarser ply yarns. When using a sweating hot plate, GoreTex® fabric showed the higher evaporation rate but still not

all the water escapes the plate and fabric immediately. After the water feed is stopped, evaporation continued briefly while the plate dries and the heat loss stays for about 200 seconds (Farnworth, 1986).

2.1.4 Protective Clothing Design

According to Easter (1994) a garment designed for occupational safety will be designed in three aspects: (1) function, (2) structure and (3) aesthetics. In the functional design process, a designer determines requirements for what the garment must or must not do functionally. The structural design of the garment determines how it is constructed or how it is put together to fulfill its function. It determines the structural lines, shapes, and parts, in addition to how they will relate to each other, how the garment will fit, and where and how it will open and close. Aesthetic design is for appearance only but it is important factor, especially with agricultural apparel. For example, if the protective garment designed to meet the needs of the farmer provides protection from toxic chemicals but is not aesthetically acceptable to the farmer, the garment will not be used except in extenuating circumstances (e.g. required by law for commercial application) (Easter, 1994). The steps in the functional design process is developed by Jones (1970):

Step 1. Request for Design.

Step 2. Exploring the Design Situation (state general objective, brainstorming, user Interview, observation literature).

Step 3. Analyzing the Critical Design Factors (observation analysis, market analysis, literature search, identification of critical factors).

Step 4. Describing the Specification (activity assessment, movement assessment, impact assessment, thermal assessment, social-psychological assessment).

Step 5. Establishing Design Criteria (charting, ranking, prioritizing).

Step 6. Developing the Prototype (material testing, technique evaluation, creative integration, solution weighted against criteria).

Step 7. Evaluation the Prototype (specification testing, user satisfaction).

Environmental and human factors are included in the critical design factors, and both factors are important for agricultural field application. Environmental factors are weather, temperature, relative humidity, and wind speed. Human factors are values, attitudes, customs, preferences, beliefs and opinions (Easter, 1994).

2.2 AGRICULTURAL CHEMICALS

Crop protection chemicals (pesticides) are biologically active compounds intended to kill pest populations by their toxic reactions. In 1987, the US Environmental Protection Agency (EPA) estimated that 814 million pounds of pesticides were in use for agriculture; 62 % herbicides, 22 % insecticides, 9 % fungicides and 1 % etc. Despite the concerns of Rachel Carsen (1962), pesticides acted to create high yields without sacrificing the environment to feed increasing global population. The rate of increase in the Third World's food production in recent years has been more than double its population growth rate. Per capita food supplies, as well as production, have continued to gain. Expense of total pesticides (excluding fertilizer and lime) has increased steadily from 3.5 to 7.7 billion dollars (USDA data from Farm Income and Expenses: 1980 to 1995). The Food Quality Protection Act (FQPA) of 1996 includes general standards for tolerances, special provisions for infants and children, and consideration of pesticide benefits. Tolerance is "safe" as defined when " a reasonable certainty that no harm will result from aggregate exposure", including all exposure through diet and other non-occupational exposure, including drinking water, for which there is reliable information. It also distinguishes between "threshold" (non-cancer causing) and "non-threshold" (cancer causing) effects consistent with EPA practice.

2.2.1 Pesticide Class and Formulations

Pesticides are classified into sixteen different categories: acaricide, bactericide, earthworm killer, fungicide, plant growth regulator, herbicide, insecticide, algicide, molluscicide, nematicide, rodenticide, synergist and other additives, attractant, virucide, wound protectant and repellent (Kidd and Hartley, 1988). There are thirteen common formulations: sprays, dusts, aerosols, granulars, fumigants, impregnates, fertilizer combinations, emulsifiable concentrates, baits, slow-release, repellents, attractants, and systemics (Kidd and Hartley, 1988). Commercial pesticides are generally complex mixtures of the pesticidal active ingredient and the inert components such as carriers. For liquid emulsion concentrates, surface agents, antifoam, emulsifier and other adjuvants are often added. The diluted liquid emulsifiable concentrate is the most common form of the pesticides used by farmers and for aerial spraying. Sprayable formulations are emulsifiable concentrates (EC), aqueous suspensions (AS), or flowables (F), wettable powders (WP), water dispersible granules (WDG), or dry flowables (DF), and solutions (S) (Hudson and Tarwater, 1988). Liquid formulations have been desirable because they disperse well in water and can be

handled easily (pumping, measuring, etc.). Nonsprayable formulations include granules, dusts, briquettes, pellets etc., which are applied directly without dilution in water. Guidelines to select protective clothing material challenged by approximately 450 potentially hazardous chemicals of interest are now available (Forsberg et al., 1989 and 1995, Johnson, 1989, and Schwope, 1989). Many of these have been categorized with respect to their relative resistance by pure compounds. However, in many actual response situations, variety of chemical mixtures (e.g., pesticides) may be encountered. The effects of one or more components of these mixtures on the protective clothing or glove materials have not been well studied. Recent research of Ehntholt et al. shows that xylene aromatic solvents were most dramatic in decreasing the breakthrough times of both carrier solvent and active ingredient, and increasing the cumulative amount of permeants measured by ASTM F739-85. Chemical mixtures show earlier breakthrough times and higher permeation rates than the pure components when used to challenge some protective glove materials (Que Hee, 1989).

2.2.2 Atrazine

Atrazine (2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine) is a widely used selective herbicide for the control of broadleaf and grassy weeds in many crops including corn, sorghum, sugarcane, maize, and pineapple. According to the 1996 Agricultural Chemical Use Estimates for Restricted Use Pesticides by United States Department of Agriculture, the herbicide atrazine was the most widely used pesticide on any crop. Seventy one percent of the corn acres were treated with atrazine (Table 2.2). Introduced to the marketplace in 1969, approximately 75 million pounds are applied each year through the U.S. corn-belt for control of a variety of annual broadleaf and grass weeds (U.S. EPA, 1994). Due to its persistence and its application for more than three decades, atrazine and its metabolites have been detected in rain, ground, and surface water. The accumulation of atrazine residues in soil may lead to the contamination of ground water (Hofmann et al., 1995). Because of its widespread application, its solubility in water, and its persistence in the environment, atrazine has become a common pollutant in the United States (Agricultural Chemicals in Ground Water, Proposed Pesticide Strategy, EPA, 1987) and Europe (Fielding et al., 1989). Properties of atrazine are shown in Chapter III. Acute oral LD_{50} for rats is about 1750 mg per kilogram. Atrazine is degraded slowly in the soil as indicated by a half life of ca. 60 day.

Table 2.2 Atrazine Usage for Field Crops in 1996

Crop	Total Area (million acres)	Applied Area (%)	Rate per Application (lb/acre)	Total Applied (1,000 lbs)
Corn	70.3	71	0.99	53466
Winter wheat	28.5	1	0.68	157
Corn, Sweet, Fresh	0.15	53	1.08	88.4
Corn, Sweet, Proc.	0.42	58	0.78	206.1
Total price = 53917.5 (1,000 lbs) x 3.6 ($/lb) =19.4 (million $)				

* Agricultural Chemical Usage, 1996 Restricted use Pesticides Summary, December 1997

* Agricultural Chemicals: Prices Paid, With Comparisons, United States, April 1992-1995

2.2.3 Chlorpyrifos

Chlorpyrifos [o,o-diethyl o-(3,5,6-trichloro-2-pyridyl) phosphothioate] is a broad-spectrum organophosphorous insecticide used to control soil insects and some foliar insect pests on a wide range of crops including strawberries, vegetables, sugar beets, cotton, citrus, coffee, maize, rice, potatoes, asparagus, greenhouse and outdoor ornamentals, mushrooms turf, as well as in forestry. It is used to control insect pests in stored products, household insect pests (including ants and larvae), and it is used as an animal ectoparasiticide. Total chlorpyrifos usage during the 1996 for agricultural crops applied 28.5 million acres was about 65,000 pounds (Table 2.3). An estimated 7 to 11 million pounds of chlorpyrifos are produced each year in the United States for domestic use. Extensive and unusual birth defects, including central nerve system, eye lip, heart in four children who were exposed in utero to chlorpyrifos (Dursban®), were reported (Janette, 1996). Similarities in defects were reported EPA documents in test animals and children exposed to Dursban®. Spray workers exposed to 0.5 % chlorpyrifos emulsion in field trials for malaria control showed decreased plasma and erythrocyte ChE (Cholinesterase) activity levels (Eliason at al., 1969). In this study, five of seven sprayers showed more than a 50% reduction in ChE within 2 weeks after spraying began. Data from five office workers exposed to chlorpyrifos in the air (levels not reported) for 5 to 21 hours over a 3-day period showed erythrocyte ChE levels were significantly ($p<0.01$) reduced after one month exposure (Hodgeson et al., 1986). Long-term exposure of chlorpyrifos showed that plasma ChE was significantly ($p<0.001$) inhibited in a group of 17 workers exposed occupationally to a Time-Weighted Average (TWA) of 7.54 mg chlorpyrifos/m^3 for 8 hours/days/week, for 2 years, when compared to age- and sex-matched controls (Hayes et al., 1980). Most workers experienced headache and complained of aggravated nasal or respiratory problems. General physical examinations were normal, however, as were erythrocyte ChE activity levels. Properties of chlorpyrifos are shown in Chapter III. Acute oral LD_{50} for rats is about 100 to 350; dermal LD_{50} for rabbits is 1000 to 2000 mg per kilogram. Since half-life of chlorpyrifos is ca. 60-120 days to 3,5,6-trichlori-pyridin-2-ol, it is degraded slowly in the soil. The mode of action of chlorpyrifos is to inhibit acetylcholine esterase which regenerates the neurotransmitter (acetylcholine). It is difficult to remove from contaminated work clothing (Laughlin et al., 1988). Some previous research shows chlorine bleach soaking pre-treatment effectively removes chlorpyrifos from cotton (Perkins et al., 1992). Less than 0.1 % chlorpyrifos residue remained on both cotton and polyester/cotton when a bleach soak pre-treatment was used with dilute chlorpyrifos (1.0 % A.I.). However, when a single wash without

Table 2.3 Chlorpyrifos (Insecticide) Usage for Field Crops in 1996

Crop	Total Area (million acres)	Applied Area (%)	Rate per Application (lb/acre)	Total Applied (1,000 lbs)
Winter wheat	28.5	1	0.43	65
Total price = 65 (1,000 lbs) x 12.325 ($/lb) =0.8 (million $)				

* Agricultural Chemical Usage, 1996 Restricted use Pesticides Summary, December 1997

* Agricultural Chemicals: Prices Paid, With Comparisons, United States, April 1992-1995

the bleach presoak was used, approximately 40 % of chlorpyrifos residue remained on the cotton fabric, and 28 % on the polyester/cotton blend. When pesticide concentrate contaminated the fabrics, approximately 38 % residue remained even through the bleach/soak pre-treatment was used. Perkins et al. suggested that if work clothing is contaminated with concentrated chloypyrifos, it should be discarded properly rather than being laundered.

2.3 LABORATORY TEST METHODS

There are three methods of fabric contamination by pesticides; drop methods, field studies and laboratory spray systems. Drop methods apply a known amount of pesticide to the sample fabric using a pipette, which is most useful to simulate the spill or mixing situations of pesticide contamination. In a field study, gauze pads are applied as a collecting material attached under a garment during actual field applications and analyzed later. The problem with the field study is that it can not produce reproducible results due to the complicated natural conditions, such as wind speed, temperature, drop size and the direction of the wind. Laboratory spray systems allow controlling droplet size as well as the amount of pesticide delivered to the fabric.

2.3.1 Drop Absorbency

Drop absorbency is performed according to the AATCC test method 79-1983. A drop of distilled water or pesticide solution is delivered from a burette on the taut surface of the fabric mounted in an embroidery hoop. The time for the specula reflection of light to disappear from the surface of the flattened drop was recorded in seconds. The drop absorbency test considers the wetting characteristics of fabric. This method provides for application of a controlled amount of pesticide in a reproducible manner. The droplet method is most closely to simulate the situation that occurs during mixing, clean up, and spill situations of pesticide.

2.3.2 Wicking

Wicking levels are determined in both warp and filling directions in fabrics by allowing a 2.5 x 15 cm specimen to hang vertically above a distilled water or pesticide solution reservoir. The weighed specimen was immersed 1 cm into the liquid, which was taken as the starting line. The wicking height after 1 min, 5 min and 10 min was recorded in centimeters. Wicking is the spontaneous flow of a liquid by capillary forces.

2.3.3 Spray Test

Agricultural protective clothing must provide a barrier against dust, pesticide particulate, and liquid penetration of pesticides during spraying, which is the most common agricultural field activity. There are three methods of fabric contamination by pesticides; drop methods, field studies, and laboratory spray systems. Drop methods apply a known amount of pesticide to the sample fabric using a pipette, which is most useful to simulate the spill or mixing situations of pesticide contamination. In a field study, gauze pads are applied as a collecting material attached under a garment during actual field applications and analyzed later. The problem with the field study is that it can not produce reproducible results due to the complicated natural conditions, such as wind speed, temperature, drop size, and the direction of the wind. A common method of exposing fabric to pesticide solution is a laboratory spray method. Orlando (1981) used a spray system and multi-layer fabric samples. The layers were then quantified to measure the amount of pesticide at each layer, thus penetration can be determined. Laboratory spray systems allow controlling droplet size as in field studies while controlling the amount of pesticide delivered to the fabric as in the drop methods (Leonas et. al, 1988). The droplets formed from a spray nozzle, more closely simulates the actual field condition of a pesticide spray impinging on the test fabric. The spray chamber is made of plexiglas and installed in the laboratory hood, which provides better operator protection, control the environmental conditions, and easier monitoring of spray motions. Orlando (1981) recommended using cotton and cotton polyester knit T-shirt fabrics to simulate the layers an agricultural worker might wear. These fabrics have been found to be as effective as the cheesecloth for the collective layer.

2.3.4 Weight (Pressure) Test

Simple simulated in-use tests on protective clothing products, such as leaning with the forearm or elbow on a 0.040 N/m (40 dyne/cm) synthetic blood soaked gauze surgical sponge, have determined the liquid-proof level of protection against microbiological challenge. The pressure applied to the medical garment was 124 KPa (18 psi) based on an orthopedic bone drill pressed into the upper abdomen of a surgeon (Beck, 1981). Investigations by Brown about applied pressures involving pressing and leaning activities with the forearm and elbow, the range was from less than 6.9 KPa (1.0 psi) to more than 345 KPa (50 psi). The NFPA (National Fire Protection Association) 1992 Standard involved one hour time of the test with a one minute 13.8 KPa (2.0 psi) pressure pulse (NFPA 1992, Liquid Splash-Protective Suits for Hazardous Chemical

Emergencies). Time periods greater than one hour did not increase bacterial penetration through barrier materials when very low pressure is applied. Lower surface tension liquids will penetrate barrier materials more easily than higher surface tension liquids. Even through the purpose of weight application is to measure the barrier efficiency against the microorganisms, it still provides a good test method against the liquid-proof simulated elbow or forearm pressures. In this study, a 2 psi weight is used for one minute as an in-use test to simulate an elbow or a forearm pressure after spraying test. This allows the protective clothing to estimate how elbow or forearm pressures affect the pesticide penetration when using actual field spray application.

2.4 THEORETICAL FACTORS THAT AFFECT HAZARDOUS CHEMICAL

The barrier property of a fabric refers to the fabric's ability to prevent (or inhibit) the movement of a chemical through the fabric (Billing et al., 1988). Two basic concepts are used to describe this movement, penetration, and permeation. These terms have been defined by ASTM Sub committee F23.30 on Chemical Resistance, Subcommittee of ASTM Committee F-23 on Protective Clothing (Henry III, 1989).

2.4.1 Penetration

The ASTM F-23 Committee has defined penetration as the "flow of chemicals through closures, porous materials, seams, and pinholes, or other imperfections in a protective clothing material on a nonmolecular basis." According to the Washburn equation (MaBain, 1950), the rate of liquid entry into a capillary related the rate of liquid penetration. Factors affecting liquid penetration were viscosity and surface tension of the liquid, as well as the pore radius, depth of the barrier, and the contact angle made by the liquid with the surface.

Washburn equation

$$V = \frac{r\nu \cos\theta}{4l\eta}$$

Where V = rate of entry of a liquid into a capillary

r = radius of the pore in the barrier

ν = surface tension of the liquid

θ = contact angle on the surface of the barrier

l = the length or depth of the pore

η = viscosity or resistance to flow of the liquid

Therefore, the barrier resistance to penetration increases when

- The liquid has a high surface tension
- The liquid viscosity is high
- The liquid makes a high contact angle with the surface
- The material is thick and has a small pore radius
- The pressure on the liquid decreases

The time at a given pressure is short, and vise versa.

With a liquid at a given surface tension, rougher surfaces are more easily wet when the resultant contact angle between liquid and solid is low.

2.4.2 Permeation

Permeation is the "process by which a chemical moves through clothing on a molecular level." Porosity refers to the degree of permeability of a material in terms of pore radius and depth. If all other things are equal, the larger the pore radius, the more rapidly liquid will penetrate it. Since pores in a given fabric are not the same size, pore size distribution is more related to the repellency than either maximum pore radius or the number of pores, unless the range of size distribution is quite narrow. While air permeability is only one factor that can influence the wearer's comfort, a larger number of very small pores can "breath" and will often make materials more comfortable to wear. The mechanism of permeation involves three steps: (1) the absorption of individual molecules of the chemical into the exposed surface of the material, (2) the molecular diffusion through the material matrix along a concentration gradient, and (3) the desorption of the chemical from the inside surface (Billing et al., 1988). Permeation testing is usually employed on textiles that are intended to protect against the diffusion of hazardous gases and vapors. The basic equation for diffusion can be drived from Fick's law, stated follows (Brown, 1995):

$$\frac{m}{A} = \frac{\Delta c}{R}$$

where m = mass flow

A = area

Δc = concentration difference

R = resistance to diffusion

If penetration can occur through the interstices between the yarns/fibers in a textile or through the pores in a porous film reinforcement, then permeation can also occur. However, the rate of transfer will most likely be more dependent on bulk flow rather than diffusion (Brown, 1995). Microorganisms are thought to penetrate and not permeate through materials due to their large size of in comparison to gas and vapor molecules (Brown, 1995). Even the smallest viruses are two orders of magnitude larger in diameter (0.025 μm) than the molecular diameters of carbon dioxide and water vapor (0.0004 μm). This size difference is the one of the reasons why monolithic (nonporous) film can act effectively as microbial barriers. This is also one of the reasons to create "breathable" monolithic film reinforcements, as the small size of water vapor allows it to diffuse through on a molecular level, while microbes are excluded due to their larger size (Brown, 1995). Most micropores are ranging in size from 0.01 to 10 micrometer.

2.4.3 Comfort

Comfort can be defined as the state that exists when the body's energy production and its exchange with its environment are in balance (Tanner, 1979) From a physiological point of view, this balance should maintain the skin at a temperature of 93° + 3° F and a relative humidity at the skin surface of less than 100%, i.e. no liquid water on the skin surface. Breathability is the ability of clothing to allow the transmission of moisture vapor by diffusion and therefore facilitate evaporative cooling. Woodcock expressed the concept of comfort as the balance of energy exchange by following equation (Tanner, 1979):

$$H = \frac{Ts - Ta}{I} + \frac{Ps - Pa}{E}$$

Where H = Total rate of heat transfer per unit area

Ts = Skin temperature

Ta = Ambient temperature

I = Insulation of clothing plus ambient air

Ps = Water vapor pressure of ambient air

Pa = Water vapor pressure of ambient air

E = Resistance to moisture vapor transmission of clothing and overlying air layer

In this formula, H, Ts and Ps are controlled by the individual subject (or physiological parameters), Ta and Pa are controlled by the environment, and I and E are controlled by the clothing and overlying air layer (Tanner, 1979). The comfort is measured by Moisture Vapor Transmission Rate (ASTM E96). The level of moisture vapor transmission required for the comfort of a resulting subject is 350 to 600 grams of moisture vapor /M^2/24 hr (Gohlke and Tanner, 1976). Under conditions of exertion and high environmental temperature, this requirement can exceed 2500 gm/M^2/24 hr, and there are conditions where comfort simply cannot be achieved (Gohlke and Tanner, 1976). A realistic minimum goal for moisture vapor permeability is 2500 gm/M^2/24 hr. This value should provide comfort under most conditions in which outerwear will be worn.

2.4.4 Wetting and Wicking

Wettability is defined as the initial behavior of the fabric, yarn, or fiber when brought into contact with liquid, and wickability is defined as the ability to sustain capillary flow. Wetting is the displacement of a fiber-air interface with a fiber-liquid interface. Drop absorbency measures the ability of a fabric to transport water from the surface into the interior of the fabric. It is greatly related to contact angle and affinity of solid and liquid properties. Hydrophobic or hydrophilic chemical nature of fiber is related to the liquid, and the morphology of their structural or physical characteristics. According to the Lisa (1987), the contact angle nature is determined by the independent interfaced tensions between air, liquid, and solid. The surface free energy of the fiber is " a measure of the ability of a fiber to adhere to itself " (Branson, 1980). Wicking is the spontaneous flow of a liquid in a porous substrate, driven by capillary forces, which affected by gravitational forces because it is related to horizontal liquid transport. The capillary reaction of liquid onto inter-fiber and yarn is an important factor. A smaller capillary radius may promote movements of liquid than larger capillary radius because larger capillary increases the liquid

holding capacity rather than transporting. Hydrophilic fibers such as cotton exhibit good wicking because as the fiber absorbs liquid in its interior, causing swelling of fiber, the inter fiber and inter yarn capillaries decrease in diameter, hence an increase in the capillary action. On the other hand, closely packed fiber structure such as woven would decrease inter-fiber and inter-yarn. The combined action of fiber swelling and closely woven constructions would increase the wicking characteristics of fabric. This explains the higher wickability of cotton broadcloth compared to twill or poplin (Raheel, 1985). Therefore, fiber or yarn structure and fabric construction is important as well as liquid viscosity and surface tension. Based on the extent of interactions with fibers, wicking processes can be divided into four categories according to Kissa (1996).

- Wicking of a liquid--no significant diffusing into the fiber surface, e.g., a hydrocarbon oil wicking in a polyester fabric at ambient temperature. Capillary penetration is the only process operating.
- Wicking accompanied by diffusion of the liquid into fibers or into a finish on the fiber--e.g., water wicking in a cotton fabric and diffusion into fibers, water wicking in a cotton fabric and diffusing into fibers, water wicking in a soil-release treated polyester fabric and diffusion into the finish. Two simultaneous processes are operating-capillary penetration and diffusion of the liquid into the fibers.
- Wicking accompanied by adsorption on fibers--e.g., an aqueous surfactant solution wicking in a polyester fabric. Several processes are operating simultaneously--capillary penetration of the liquid, and adsorption of the surfactant of fibers.
- Wicking involving adsorption and diffusion into fibers--e.g., an aqueous surfactant solution wicking in a cotton fabric. Several processed are operating simultaneously--capillary penetration, diffusion of the liquid into the fibers, diffusion of the surfactant in the liquid, and adsorption of the surfactant on fibers.

CHAPTER III

METHODOLOGY

The experimental design of the research project is reported. The fabrics, including nonwoven, woven and knit materials, are described. The pesticides used in conducting experimental design are described. The physical tests are reported. The equipment used in this study to contaminate the fabrics is described and evaluated. This chapter includes a description of sample preparation, sample contamination, the application of an externally applied weight to the pesticide contamination, extraction and analyses. Weight (2 psi, 1 min) was applied to the chemically contaminated sample. Two different analytical methods, gas chromatography (GC) and high performance liquid chromatography (HPLC), were used to analyze pesticide extraction. The methods of image analysis of fiber and web characteristics are reported, and finally, the statistical analysis is included in this chapter.

3.1 FABRICS

To determine the barrier efficiency against liquid pesticides, six different types of fabric were used in this study: four types of nonwoven material, 100 percent T-shirt cotton knit, and cotton denim twill weave. Fabrics were chosen to compare the variables of fabric characteristics: fiber content (cotton or polyolefin), constructions (nonwovens, woven, knit) and combination methods (spunbond-meltblown-spunbond, microporous film laminated spunbond, nonporous film spunbond, flash spun polyethylene) of nonwoven materials. Cotton knit and denim were supplied from TESTFABRICS. Four types of nonwoven materials, commercially used as protective clothing, were supplied from Kappler® Protective Apparel & Fabrics. Tyvek®1422 is one of Du Pont®'s products. The descriptions and the characteristics of the fabrics are shown in Table 3.1 and 3.2. The characteristics of the fabrics were determined using Standard Test Methods. Thickness (D1774-64), Mass Per Unit Area of Woven Fabrics (D3772-85), Air Permeability (D737-75), Yarn Count (D3775-85) was determined using ASTM, and Hydrostatic Water Resistance (127-1985) was determined using AATCC test method.

Table 3.1 Fabric Descriptions

Fabric Code	Trade Name or Style No.	Fiber Content	Construction	Finish
SMS	Pro/Shield ®1[a]	100% Polypropylene	Nonwoven (Spunbond/meltblown/ spunbond)	Anti-static
MSB	Pro/Shield ®2[a]	100% Polypropylene	Nonwoven (Microporous film spunbond)	Anti-static
CSB	Pro/Shield ®3[a]	100% Polypropylene	Nonwoven (Coated spunbond)	None
Tyvek®	Tyvek®1422[b]	100% Polyethylene	Nonwoven	Anti-static
Cotton	437W[c]	100% Cotton	Cotton single knit	None
Denim	Blue denim[c]	100% Cotton	Woven-twill (2 plies, twisted Z direction)	None

a. Kappler® Protective Apparel & Fabrics, Guntersville, Alabama.

b. Du Pont® 15 Stern Avenue, Springfield, New Jersey

c. TESTFABRICS, Inc., 200 Blockford Avenue, Middlesex, New Jersey

Table 3.2. Fabric Characteristics

Fabric	Weight (g/m^2)	Thickness (mm)	Air permeability ($m^3/min/m^2$)	Hydrostatic Water Resistance (cm) Face / Back		Yarn or Loop Count (yarns/cm) Warp / Fill	
SMS	61.0	0.4462	21.5	57.4	50.7	NA[b]	NA
MSB	57.6	0.3984	NA	NA	103.8	NA	NA
CSB	61.0	0.3758	NA	NA	81.3	NA	NA
Tyvek®	40.7	0.1992	NA	101.8	93.5	NA	NA
Cotton	139.0	0.6022	41.5	20.8 (47.0)[a]	19.0(59.9)	15	20
Denim	474.7	1.7680	4.38	20.3 (15.1)	19.6(14.10)	23	17
ASTM	D3772-85	D1774-64	D737-75	AATCC127-1985		D3775-85	

a. Measured value after laundering

b. NA means not available

3.1.1Nonwoven Materials

3.1.1.1 SMS (spunbond-meltblown-spunbond) Nonwoven

Polypropylene spunbond-meltblown-spunbond nonwoven layers were thermally point-bonded. The meltblown layer provided a soft, flexible characteristic. While the spunbond provided strength. Point bonding imparted strength and integrity while minimizing stiffness. It was treated with an anti-static finish. The basis weight of the fabric was 61.0 gram per square meter and the thickness was 0.4465 millimeter. Air permeability of the fabric was 21.5 $m^3/min/m^2$ and hydrostatic water resistance was 54.4 cm for front side, 50.7 cm for back side of the fabric, which indicated that SMS fabric had similar characteristics on both sides.

3.1.1.2 Microporous film Spunbond Nonwoven

An antistatic treated microporous (breathable) polyolefin film spunbond provided barrier protection plus comfort by allowing the evaporation of the water vapor (0.0004 μm). The basis weight of the fabric was 57.6 gram per square meter and the thickness was 0.3984 millimeter. Air permeability and hydrostatic water resistance tests of the fabric were not available. Material cost was proprietary and not publicly available.

3.1.1.3 Nonporous Film Spunbond Nonwoven

An unfinished polyolefin nonporous film spunbond nonwoven provided good protection against particles and liquids. It cost about half price per suit compared to microporous polyolefin film spunbond. The basis weight of the fabric was 61.0 gram per square meter and the thickness was 0.3758 millimeter. Air permeability and hydrostatic water resistance tests of the fabric were not available. Material cost was proprietary and not publicly available.

3.1.1.4 Tyvek®1422

Tyvek®1422 is composed of numerous layers of high-density polyethylene filaments thermally bonded together. The polymer contained typical polyolefin processing additives, such as anti-static agent, which was present at a weight concentration of less than 1.0 percent. The basis weight of the fabric was 40.7 gram per square meter and the thickness was 0.1992 millimeter. Air permeability of the fabric was 41.5 $m^3/min/m^2$ and hydrostatic water resistance was 101.8 cm for front side, 93.5 cm for back of the fabric. It was inexpensive (69 cents per linear yard) compared to the other nonwovens. It was treated with an anti-static finish.

3.1.2 Woven Material

3.1.2.1 100 % Cotton Denim

The denim was made of one hundred percent cotton and woven twill, which consisted of two plies and twisted *z* direction. Yarn count of the fabric per one centimeter was 23 for warp and 17 for fill. It costs 7 dollars per yard.

3.1.3 Knit Material

3.1.3.1 100 % T-shirt Cotton Knit

The T-shirt cotton was made of 100 % cotton and single loop knit. The number of wales of the cotton knit fabric per one centimeter was 15 and the number of courses was 20. It cost 5 dollars and 36 cents per yard.

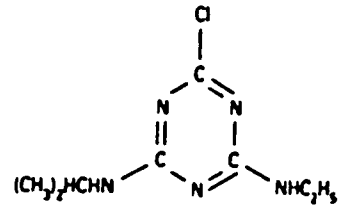
3.2 PESTICIDES

Because pesticides are composed of both active ingredients and inert carrier materials depending on their formulations, the determination of the penetrability of pesticides is more complicated. Penetration of liquid pesticides should be considered based on the composition of active ingredient, the amount of dilution and the composition of the inert materials. Two pesticides were selected in this study according to their different chemical structures, formulations and their broad applications: atrazine, triazine herbicide and chlorpyrifos, organophosphorous insecticide. They are the most commonly used commercial herbicide (atrazine) and residential insecticide (chlorpyrifos).

3.2.1 Atrazine (Herbicide)

Atrazine [2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine] is used in the control of annual broadleaf and grass weeds in corn and other crops. According to the recommendation of agricultural scientists, 2.5 % concentration active ingredient of atrazine (Atrazine 4L, herbicide), as a general concentration of atrazine in actual field applications, was selected. Atrazine 4L®, a flowable liquid concentrate formulation with a four pound per gallon concentration, was purchased from the Co-Op, Knoxville, TN. The chemical properties of atrazine are shown in Table 3.3. The MSDS for Atrazine 4L® is shown in Appendix A.

Table 3.3 Chemical and Physical Properties of Atrazine

Subject	Description
Chemical Name	2-Chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine
Chemical Structure	
Chemical Abstracts Registry (CAS) Number	1912-24-9
Chemical Formula	$C_8H_{14}ClN_5$
Molecular Weight	215.7 g/ mole
Physical State (25 °C)	Solid
Melting Point	173-175° C
Vapor Pressure (25°C)	3×10^{-7} mm Hg
Water Solubility (25°C)	33 ppm
Toxicity: Oral LD_{50} (rat)	1750 mg/kg
Soluble in	CH_3OH, $CHCl_3$
Half Life	60 days
Soil Koc*	100 g/ml
Classification by hazard	Unlikely to present acute hazard in normal use

*. The tendency of the pesticide to be strongly attached, by chemical or physical bonds, to surfaces of soil particles or organic carbon.

3.2.2 Chlorpyrifos (Insecticide)

Chlorpyrfos [o,o-diethyl 0-(3,5,6-trichloro-2-pyridinyl)phosphorothioate] is a broad-spectrum organophosphorous insecticide that is used on a wide range of cotton, asparagus, greenhouse, vegetables, potatoes, beets, and rice as well as household insect pests. According to the recommendation of agricultural scientists, 1.0 % concentration of active ingredient of chlorpyrifos (Dursban®, insecticide), was selected because it is the typical concentration of chlorpyrifos used in actual field applications. Dursban®, an emulsifiable concentrate formulation with a 0.5 pound per gallon concentration, was purchased locally (Knoxville, TN). The chemical properties of chlorpyrifos are shown in Table 3.4. The MSDS for Dursban® is shown in Appendix B.

3.2.3 Preparing Pesticide Solution

In order to obtain the proper dilution of pesticide, the following equation was used. The equation has 'Q' as the diluent and 'A' as the active ingredient. Four liters of the pesticide solution were prepared. Distilled water was used to dilute the concentrated pesticides to make four liters.

$$Q \times \frac{\textbf{Percent Concentration Required}}{\textbf{Percent Concentration of Active Ingredient}} = A$$

Atrazine 4L®:

$$4000 \text{ ml} \times \frac{2.5\ \%\ \text{Concentration of Atrazine}}{40.8\ \%\ \text{Active Ingredient}} = 245.098 \text{ ml}$$

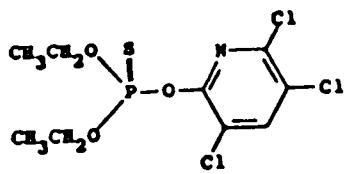
Dursban®:

$$4000 \text{ ml} \times \frac{1.0\ \%\ \text{Concentration of Chlorpyrifos}}{6.62\ \%\ \text{Active Ingredient}} = 604.230 \text{ ml}$$

3.3 SAMPLE PREPARATION

The cotton knit and denim fabrics were pre-laundered according to the AATCC (American Association of Textile Chemists and Colorists) test method 135-1978 to eliminate

Table 3.4 Chemical and Physical Properties of Chlorpyrifos

Subject	Description
Chemical Name	o,o-diethyl-o-(3,5,6-trichloro-2-pyridinyl) phosphorothioate
Chemical Structure	
Chemical Abstracts Registry (CAS) Number	2921-88-2
Chemical Formula	$C_9 H_{11}Cl_3 NO_3 PS$
Molecular Weight	350.57 g/ mole
Physical State (25 °C)	White, Granular crystals
Melting Point	41 to 43.5° C
Vapor Pressure (25°C)	1.87×10^{-5} mm Hg
Water Solubility (25°C)	0.4 ppm
Toxicity: Oral LD_{50} (rat)	100-350 mg/kg
Dermal LD_{50} (rabbit)	1000-2000 mg/kg
Half Life	30 -120 days
Soil Koc*	6070 g/ml

*. The tendency of the pesticide to be strongly attached, by chemical or physical bonds, to surfaces of soil particles or organic carbon.

unwanted finishing residue, sizing, auxiliaries and softeners applied during processing. A Maytag® washer and a Maytag® dryer were used. The temperature of the wash water was 60 °C, the rinse water was 49°C, and Tide®, a commercially available detergent, was used according to the manufacture's recommendation. The wash was a 12 minute wash cycle, with a 4 minute rinse cycle, and spin dry. The fabrics were removed from the washer and were placed into the dryer where they were tumbled dry. Fabrics were ironed. The nonwoven fabrics were used as received.

3.3.1 Multi-layer Test Sample

The multi-layer sample was prepared similarily to those used in studies by Leonas (1985) and Dimit (1989). The multi-layer samples were consisted of three layers from top to bottom as follows: barrier protective fabric (top), 100 % cotton knit (middle) and mylar film (bottom). The edges were taped with masking tape (Figure 1).

3.3.1.1 Protective Apparel Test Material (layer 1)

The barrier protective fabric, top layer, is that fabric being considered for protective apparel.

3.3.1.2 100 % Cotton Knit (layer 2)

The collector layer, middle layer, is that fabric collecting the chemical penetration. The collector layer chosen for this study was 100 % cotton knit. The cotton knit was selected because Orlando (1981) recommended using a material closely simulated undergarments worn by agricultural workers.

3.3.1.3 Mylar Film (layer 3)

Mylar (polyethylene terephthalate) film, bottom layer, is that material supporting the multi-layer sample. This layer was used to prevent liquid penetration and other chemical contamination from the under side of the sample during the application and handling. This layer was removed and was discarded after use. Each test material was cut in a 15.24 x 15.24 centimeter squared (36 in^2) and assembled to make a multi-layer sample. Double-sided tape was used to attach each layer to make a flat and tight sample without crimps. The edges of the multi-layer sample were sealed with one-inch masking tape to prevent the penetration of pesticides through the edges of the fabric so that pesticides that penetrated would be detected during analysis. Each layer was arranged and assembled with the machine direction oriented in the same direction in an attempt to obtain more consistent results. The multi-layer samples were

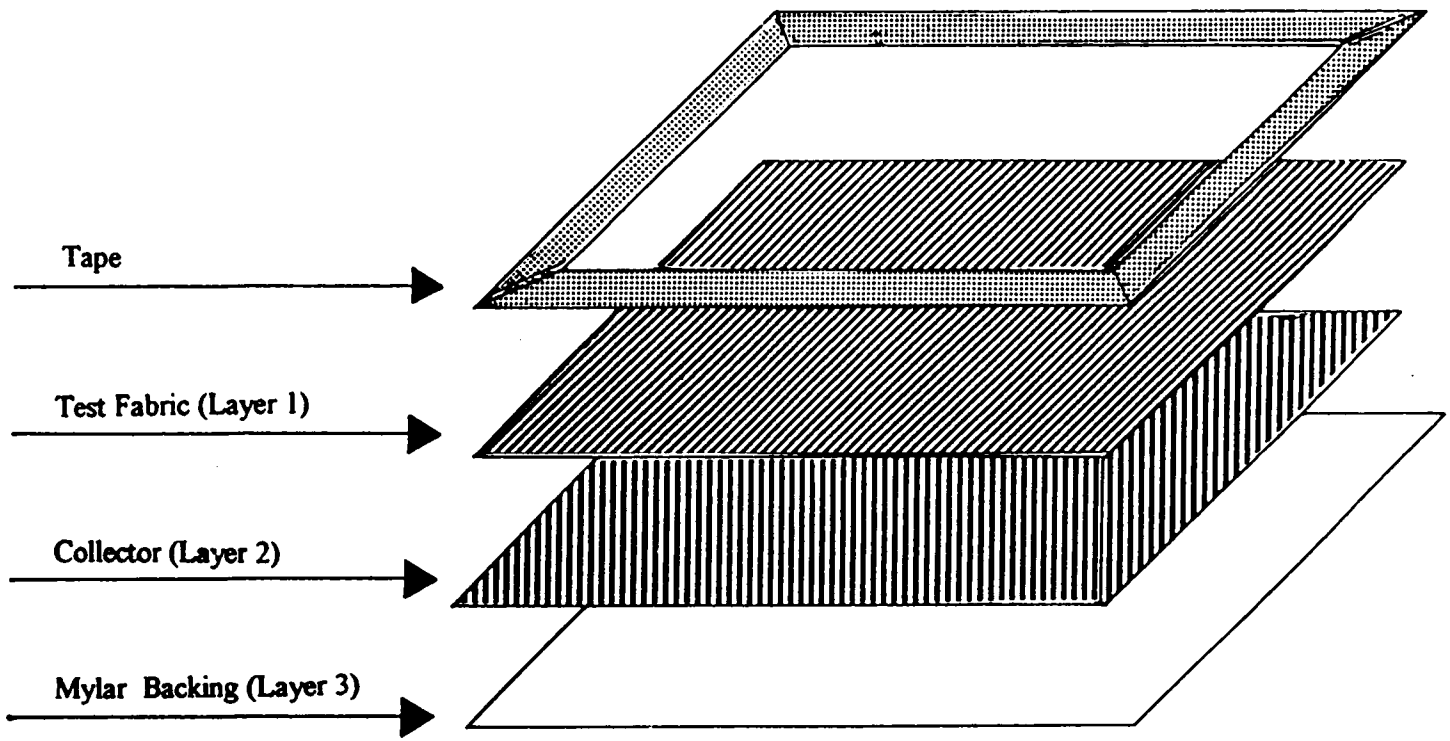


Figure 1 Illustration of Multi-layer Sample

placed in the conditioning room at least 24 hours prior to spraying at 21°C (70 ± 2 °F) with relative humidity 65 ± 5 %, according to the ASTM Practice for Conditioning Textiles, D1776-79.

3.4 CONTAMINATION OF THE FABRIC

3.4.1 Laboratory Spray Chamber Design

The laboratory spray chamber (Figure 2), designed by Leonas et al.(1985), was used to contaminate the fabrics. The spray chamber consist of

1) Sample Holder
2) Speed control box
3) Spray nozzle
4) Pressure Gauge at spray nozzle
5) Pesticide reservoir (pressurized Canister)
6) Pressure regulator on compressed air tank
8) Pesticide drainage reservoir

The dimension of the spray chamber is 115 cm (length) x 30 cm (width) x 60 cm (height). The spray chamber is made of Plexiglas and installed in the laboratory hood, which provides operator protection and easy monitoring of spray motions. The sprayer is vertical and is 90° to the fabric. There are 4 replicate positions, which allow 4 samples to be tested at the same time.

3.4.2 Evaluation of Spray Chamber

The spray chamber was evaluated to ensure consistent spray application to each test specimen location. Spray coverage uniformity and consistency in the amount of liquid delivered, were evaluated for six different types of nozzle. To select the nozzle, that would deliver the liquid most evenly across the samples, the mass balance was measured by two methods, a mass balance equation and a petri-dish. To measure the mass balance more precisely, a pressure of 10 psi was used. One nozzle was selected because the predicted mass and measured mass were similar. Because the pressure at the nozzle tip was critical, a pressure gauge (Ashcroft®, Test Gauge, 0.2 subdivision, Accuracy Grade 3A, Graingier, knoxville, TN) was attached to the end of the nozzle tip. It allowed the operator to detect and to control the pressure precisely at the moment of the discharge from the end of the nozzle tip. A stainless

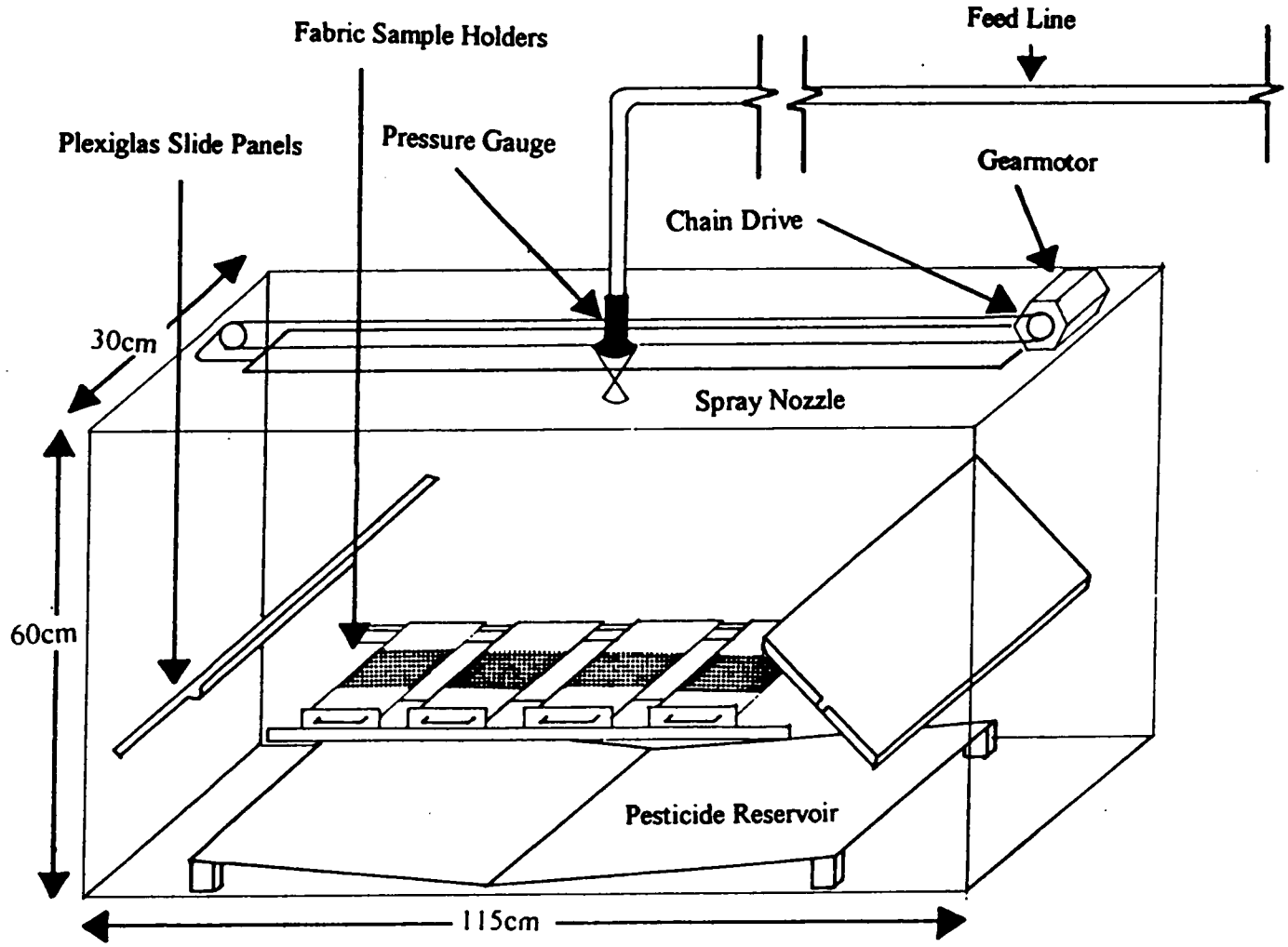


Figure 2 Illustration of Spray Chamber

steel pressure canister, served as a pesticide reservoir. Compressed air was the carrier gas used to deliver the liquid pesticide. Distilled water was used to dilute the pesticides. The pesticide solutions were mixed thoroughly before spraying. The speed of the nozzle traversing across the width of the spray chamber was measured for each direction (LR, RL) and dial setting. The speed from right to left and the speed from left to right was compared. The dial setting of 8 was selected because it provided stable data; this was considered similar to the wind speed of outside field applications (Leonas et al., 1988). According to the standard method of laboratory spray testing for agricultural application, 40 psi was selected (ASTM E 641-85).

3.4.3. Mass Balance of Theoretical Amounts of Pesticides

The mass balance of each pesticide was measured to determine the amount of pesticide that was applied to the outside barrier fabric. The theoretical mass balance was calculated. The mass balance was measured using petri dishes. The two test results were campared. A Fan Spray® 1.5GPM40 nozzle was used in this experiment based on the former test results.

3.4.3.1 Mass Balance Equation

Mass balance was measured by the mass balance equation. Factors such as flow rate, speed, and width were measured individually and the mass balance was calculated. The average speed of the mechanical movement from the left to the right was measured using a stopwatch. Flow rate was measured with a 50-ml graduated cylinder. The pressure from the nozzle tip was fixed at 40 psi. The angle from the nozzle tip and the width along the sample were measured. The distance from the end of the nozzle tip to the sample was fixed at 30.48 cm (12 inches). The theoretical mass balance was calculated by the following equation:

$$\frac{\textbf{Volume (ml)}}{\textbf{Area (cm}^2\textbf{)}} = \frac{\textbf{Flow Rate (ml)}}{\textbf{(sec)}} \times \frac{\textbf{1 (sec)}}{\textbf{Speed (cm)}} \times \frac{\textbf{1}}{\textbf{Width (cm)}}$$

The theoretical amount of pesticide applied to the 25.81 cm^2 (4 in^2) sample area was calculated. The theoretical mass balance of atrazine 2.5 % (v/v) solution and chlorpyrifos 1.0 % (v/v) solution applied on the 25.81 cm^2 (4 in^2) sample cut area and the theoretical concentration of atrazine and chlorpyrifos were calculated.

3.4.3.2 Petri-dish Test

Petri dishes were placed in the center 25.81 cm^2 (4 in^2) of each fabric sample to measure the actual mass balance of each pesticide. Atrazine 2.5 % (v/v) and chlorpyrifos 1.0 % (v/v) concentrated solutions were used. Due to the differences of liquid delivery, each sample was marked and only the center area was cut. On the each replication position a petri dish was placed on the same center position and the amounts of pesticide liquid were measured using a balance. Mass balance of 2.5 % atrazine and 1.0 % chlorpyrifos on the 25.81 cm^2 (4 in^2) area, the same as the sample cut area, was measured by using distilled water.

3.4.4 Pesticide Spray Contamination of the Fabric

For samples of test procedure A, a 25.81 cm^2 area (2 x 2 in^2) was marked in the center of each sample using a permanent marker and for samples of test procedure B, a two-inch diameter circle was added, where the 2 psi weight was placed. There were four replicate positions in the spray chamber. Each multi-layer test sample was mounted on a plexiglas board (sample holder) and the edges of the sample were secured with four clamps before the board was positioned (Figure 3). The following conditions were selected according to the preliminary tests to distribute better droplet size and uniformity: 4.809 (cm/sec), 40 psi and only one direction from left to right motion.

3.5 EXTRACTION OF PESTICIDES

After being sprayed with the pesticide, the center 25.81 cm^2 (4 in^2) square was cut immediately from each multi-layer sample with a sharp die and the layers were separated. Top and bottom were discarded. The cotton collecting material was placed in a 150-ml Erlenmeyer flask where the pesticide was extracted. The samples were covered with 25 ml methanol. Samples were shaken by a Wrist Action ®Shaker (Model 75, Burrel Instrument Co., pittsburgh, PA) at the two dial setting for 30 minutes. The 25 ml extract was decanted into a glass bottle. The samples were shaken with another 25 ml methanol for another 30 minutes. The two 25 ml extracts were combined in the glass bottle and stored in the refrigerator.

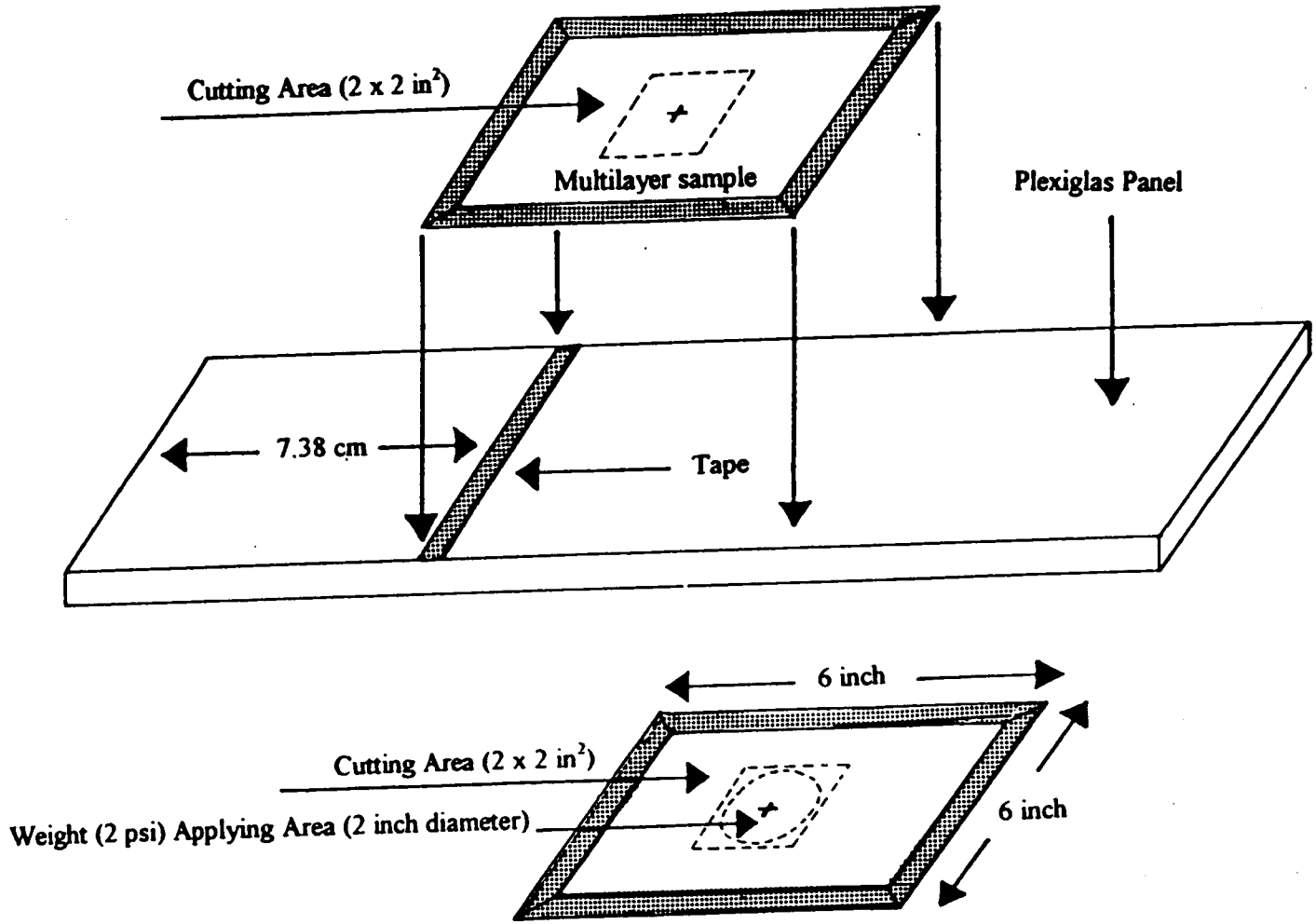


Figure 3 Illustration of Fabric Holder and Cutting Area

3.5.1 Extraction Efficiency

3.5.1.1 Spike Test

The spike test was important to calculate the percent efficiency of extraction. A known concentrate solution of pure atrazine compound was prepared in methanol (500 ppm). A repeat pipette (Ranin®) was used to deliver 1 ml of an atrazine solution onto the 25.81 cm^2 (4 in^2) surface area of cotton fabric. After spiking, samples were shaken twice in the methanol (total 50 ml) for 30 minutes each time, and then extraction solutions were analyzed using HPLC and GC. The theoretical concentration of atrazine was calculated. The percent recovery of atrazine from the cotton sample was calculated. Blank samples (cotton only) were tested using a GC and a HPLC to see whether atrazine residue was in the water used for dilutions. The instrument sensitivity was determined by measuring a series of pesticide dilutions. The sample extracts were diluted to a 1 to 100 concentration when using a repeat pipette for GC analysis but were not diluted for HPLC. The sample dilutions were transferred to a 2-ml glass vial for GC analysis.

3.6 EXPERIMENTAL DESIGN

The experimental design was prepared to conduct this research according to different test methods and different analytical methods. For test methods, without weight test and the weight (2psi, 1 min) test, and for analytical methods, GC and HPLC were used to analyze the extracts from the fabric samples. To compare the pesticide penetration (the dependent variable), extraction efficiency, accuracy, and the effect of dilution were evaluated. To determine the variation in pesticide penetration, a 6 (fabric) x 2 (pesticide) experimental design was evaluated using a GC, and a 6 (fabric) x 1 (pesticide) experimental design was evaluated using a HPLC. Six replications for each fabric in procedure A and two replications for each fabric in procedure B were evaluated by using a GC. The experimental design for the test methods is presented first, followed by the experimental design for the analytical methods. The illustration of instruments used in this study is shown in appendix C.

3.6.1 Test Methods

Two different experimental tests were designed; one was without a weight test and the other was included a weight (2 psi, 1 min) test. The replications of the study were conducted separately due to the differences of those variables and different handling of test methods. The

results of the two replications were analyzed separately and were combined using statistical analysis methods.

3.6.1.1 Without Weight Test – Test Procedure A

The independent variables examined in this test include fabric type, fabric characteristics and pesticide characteristics. The dependent variable was pesticide penetration. To determine the protection against pesticide penetration in terms of the fabric type and the different chemical class of pesticide, a 6 x 2 experimental design was used.

1) Fabrics
    a. SMS (spunbond/meltblown/spunbond)
    b. MSB (microporous film laminated spunbond)
    c. CSB (coated spunbond)
    d. Tyvek® 1422
    e. 100% Cotton Knit
    f. 100% Cotton Denim
2) Pesticide
    a. Atrazine
    b. Chlorpyrifos
3) Analysis
    a. GC
    b. HPLC

To evaluate the effect of the fabric characteristics, eight experimental characteristics were measured.

1) Weight
2) Thickness
3) Air Permeability
4) Hydrostatic Water Resistance Test
5) Fiber Diameter
6) Pore Diameter
7) Web Uniformity
8) Fiber Construction

3.6.1.2 Weight (2 psi) Test- Test Procedure B

To determine the degree of protection against pesticide penetration when pressure was applied, a 6 x 2 experimental design was used. The weight (2 psi, I min) was put on the fabric after spraying and a 25.81 cm^2 (4 in^2) square area was cut. This simulated the elbow effect according to Peter (1992).

1) Fabrics

a. SMS (spunbond/meltblown/spunbond)

b. MSB (microporous film laminated spunbond)

c. CSB (coated spunbond)

d. Tyvek® 1422

e. 100 % Cotton Knit

f. 100 % Cotton Denim

2) Pesticide

a. Atrazine

b. Chlorpyrifos

3) Analysis

a. GC

b. HPLC

The results were measured in micrograms per milliliter and converted to milligrams per centimeter squared. Percent penetrations were calculated by theoretical mass balance.

3.7 ANALYTICAL METHODS

3.7.1 Gas Chromatography (GC)

The pesticide extracts from the cotton collector fabrics were analyzed using a Hewlett Packard (HP) 5890A gas chromatography. A nitrogen phosphorous detector (NPD) and splitless injector were used. The detector temperature was 250 °C. One µl aliquots from each extract were analyzed by a DB210, 0.53 megabore, one microfilm thick column. The pressure at the column head was 50 KPa and the oven temperature was 150 °C. Helium was used as a carrier gas to move the compounds through the column.

3.7.2 High Performance Liquid Chromatography (HPLC)

In this analysis, Waters HPLC, Maxima 820 and a multi wavelength detector, Waters 490 E were used. For atrazine, 223 nm uv was chosen and an HP ODS Hypersil, 5μm, 100 x 4.6 mm column was used. Helium gas was used for the purge gas. The injection volume was 15 μL. The composition of the ternary eluent mixture was water (45 %), acetonitrile (45 %), and methanol (10 %). Flow rate was 1.5 ml per minute.

3.7.3 Standard Calibration Curve

HPLC calibration curve was measured. Analytical grade pesticides were used. Atrazine (98 percent pure active ingredient), and simazine, as an internal standard of atrazine (99 percent) were purchased from Chem Service. A stock solution was made from 50 mg of atrazine in 50 ml of methanol, and then a series of eight concentrations of the analytical standards were prepared from the stock solution. Three repeats of each of the eight standards were analyzed by using HPLC. The correlation, the intercept, and the slope of the standard calibration curve were calculated.

3.8 STATISTICAL ANALYSIS

To determine the effectiveness of a fabric as a barrier to pesticide penetration, the amount of pesticide collected on the middle cotton knit layer of the multi-layer sample was considered. The data used in the statistical analysis was based on the micrograms of pesticide extract per milliliter of methanol, analyzed using a GC and a HPLC. Variables included six fabrics, two pesticides and with or without pressure (2 psi). Since the different active ingredients of atrazine and chlorpyrifos were applied, each procedure was analyzed separately by pesticide.

Hypotheses of statistical analysis are:

1. Different fabrics provide different degrees of protection against pesticide penetration.
2. Different pesticides have different penetration characteristics.
3. The pesticide chemical class is responsible for different behaviors of the penetration of the pesticide.
4. The application of an externally applied weight (2 psi, 1 min) to the pesticide contaminate fabric affects the degree of pesticide penetration.

5. Web uniformity influences pesticide penetration.

First, the general linear model (GLM) was used to determine whether there were significant differences of penetration for fabric type, instrument type, or weight application type in the different pesticides. In the case of chlorpyfios, fabric SMS was excluded to adjust the normal distribution. To evaluate the data between two independent variables, such as instrument type or weight application, the Mann-Whiteney, and to evaluate more than two independent variables, such as different types of fabric, the Kruskai-Wallis different non-parametric test methods were used. Second, to determine whether two groups had different means of a continuous variable such as:

(a) Atrazine penetration (ppm) without weight/weight using a GC

(b) Chlorpyrifos penetration (ppm) without weight/weight using a GC

(c) Atrazine penetration (ppm) without weight/weight using a HPLC

(d) Atrazine penetration (ppm) without weight GC/HPLC

(e) Atrazine penetration (ppm) weight using GC/HPLC

(f) Atrazine and chlorpyrifos penetrations (%) without weight using a GC

(g) Atrazine and chlorpyrifos penetration (%) with weight using a GC,

t-test was used as assuming that the variables were independent from a normal distribution. Before the t-test, to determine if two groups were from the same variance of a population group, the "Levene's test for equality of variances" was used. If the variables in the two groups were different, the unequal variance t-test was used. To compare the penetration and barrier efficiency between the atrazine and chlorpyrifos, percent penetration (%) was used. T-tests of equal variances were reported separately by individual fabric type. Eventhough the t-test was a more powerful statistical analysis than the non-parametric test, non-parametric tests were performed for some samples. The non-parametric tests were done on samples that had such a small sample size that they were not normally distributed because they had unequal variances. The results from non-parametric tests were compared to those results of the t-tests. To evaluate the data between two independent variables, the Mann-Whitney test was performed. To verify the degree of significance, the Monte Carlo p-value, having a 99 % confidence interval, was reported. Original data was used without any transformation since the value of the power estimation was close to one (1.15). The statistical analysis was performed using SPSS software version 7.5. Linear regression analysis was performed in the calibration curves.

And other hypotheses are compared and discussed using by GLM statistical analysis:

1. As fabric weight increases penetration decreases.
2. As fabric thickness increases penetration decreases.
3. Air permeability increases penetration decreases.
4. Hydrostatic water resistance test can be used to predict the ability of the fabric to prevent pesticide penetration.
5. Fabric functional finish influences pesticide penetration.
6. Fabric construction influences pesticide penetration.

3.9 IMAGE ANALYSIS

Image analysis was used to determine fiber diameter, pore diameter and fiber web uniformity of nonwoven fabric layers. A microscope was used to form an image of each web. The video camera produces a standard RS-170 analog video signal with 550 lines of resolution. The frame grabber is a plug-in board, which digitizes the video signal with 8-bit gray level resolution (256 gray levels) and 640 x 480 spatial resolution. The computer was an IBM compatible personal computer with a Pentium processor and the WebPro ® 2.0 software was used.

3.9.1 Fiber Diameter

The individual layers of the four different nonwovens: spunbond/meltblown/spunbond (SMS), microporous film laminated spunbond (MSB), coated spunbond (CSB) and Tyvek® were carefully separated before image analysis. Only fiber diameters of spunbond could be accurately measured due to the image analysis equipment being limited to nonwovens with a maximum basis weight of 33.9 gram per square meter (1oz/yd^2). Fiber diameters in the SMS and CSB were determined from 30 fibers; and 50 fibers were measured in the MSB. The mean (X, μm), coefficient of variation (CV, %), minimum (Min, μm) and maximum (Max, μm) of the fiber diameters in the spunbond fabrics were calculated by the WebPro® 2.0 software.

3.9.2 Pore Diameter

The pores in a 3.3 mm^2 area were imaged by the WebPro® software. Only pore diameters of spunbond could be accurately measured since the image analysis equipment is limited to nonwovens with a maximum basis weight of 1 oz/yd^2. Pore diameters in the MSB and

CSB were determined from 10 fibers. The mean (X, μm), coefficient of variation (CV, %), minimum (Min, μm) and maximum (Max, μm) of the pore diameters in the spunbond fabrics and the percent pore coverage of the sample area were calculated by the WebPro® software.

3.9.3 Fiber Web Uniformity

Fiber web uniformity was determined without separation of the layers of the nonwovens because a different light source was used to shine the light through the web. The Web in a 825mm^2 area was imaged by the WebPro® software. Spunbond/meltblown/spunbond (SMS), microporous film laminated spunbond (MSB), coated spunbond (CSB) and Tyvek® were measured without separation. The web was illuminated from the bottom, which scattered the light. The machine direction (MD) and the cross direction (CD) of the fabric were measured separately. The minimum number of pixels was 25 and the maximum number of pixels was 5,760,000.

CHAPTER IV

RESULTS AND DISCUSSION

4.1. EVALUATION OF SPRAY CHAMBER

Six different types of nozzle were evaluated to ensure consistent spray application. Spray coverage uniformity, consistency in the amount of liquid delivered, and the distribution of droplets was measured for each of the six different types of nozzle (Table 4.1). To control the pressure more precisely at the moment of the discharge from the end of the nozzle tip, the spray test was conducted under low pressure, 10 psi, and then the flow rate was converted to 40 psi. For each nozzle, the center portion of the spray was more concentrated than the spray was at the outer edges. For most nozzles, there were big differences between the theoretical flow rate and the measured flow rate. As a result, a pressure gauge was purchased and attached to the end of the nozzle tip. Based on the test results, a Fan Spray® 1.5GPM40 nozzle was selected because it had a uniform droplet and the measured and calculated mass balance were similar. The 0.23GPM72 and 0.33GPM65 nozzles produced big droplets that were discharged irregularly when the nozzle moved across the width of the spray chamber. The 1.5GPM80 and 2.0GPM80 nozzles discharged a larger amount of liquid and their angles were about twice as large as those obtained from the 1.5GPM40 nozzle. These two nozzles were rejected for used in this study because their spray saturated the fabrics resulting in an excess of pesticide that flowed uncontrollably i.e. off and under the sample. The spray angle from these two nozzles was so large that the spray hit the spray chamber walls above the sample and then bounced off the wall onto the samples below. This collision of the spray and the wall was not reproducible and therefore, these nozzles were rejected. A petri dish was put on the center area of each sample to evaluate the differences in the amount of liquid spray (Table 4.2). The rate of traverse was measured in both direction and for each dial setting of the control box. The evaluation of the speed is shown in Table 4.3. The data indicated that the rate of traverse was not the same for each direction. Therefore, only the spray from the nozzle as it moved from the left to the right, was chosen. The dial setting eight was selected because it moved rapidly preventing pesticide liquid from saturating the samples and it was reproducible. Dial setting eight provided a wind speed similar to outside testing field applications,

Table 4.1 Evaluation of Six Different Types of Nozzle

Nozzle Name	Theoretical Angle (°)	Theoretical Flow rate (ml/sec)	Measured Flow rate (ml/sec)	Spray Type	Width (cm)	Tan θ	Actual angle(°)	Volume/Area (ml/cm^2)
.23GPM72	72	14.509	50.800	Fan	56	0.9167	85.02	0.17967
.33GPM65	65	20.817	3.506	Flat	30	0.5000	53.14	0.02273
1.5GPM40	40	94.625	18.962	Fan	25	0.4167	45.24	0.14754
2.0GPM40	40	126.166	23.358	Fan	25	0.4167	45.24	0.18174
1.5GPM40	80	94.625	19.066	Fan	18	0.2917	32.52	0.21192
2.0GPM80	80	126.166	26.246	Fan	17	0.2708	30.30	0.31417

Tan θ =[(width, cm/2)/ height, 30.48 cm], $\theta = \tan^{-1}$ [(width, cm/2)/height, 30.48 cm)], Actual angle = 2θ
Pressure: Actual experiment was conducted at 10psi and was converted to 40 psi
(Flow rate is function of square root of Pressure) and measured by using a 500-mL graduated cylinder
Rate of traverse: 5.06 cm/sec
(Volume, lm/Area, cm^2) = flow rate (ml/sec) x (sec/speed, cm) x (1/ width, cm)

Table 4.2 Petri-dish Test

Nozzle Name	Volume/Area (ml/cm^2)	Volume/Area (ml/cm^2) using a petri dish (5.08 cm diameter)	Differences of Volume/Area (ml/cm^2) between the center and average parts (C-A)[a]
.23GPM 72	0.0898	0.1213	0.0315
.33GPM 65	0.0114	0.0199	0.0085
1.5GPM 40	0.0738	0.0930	0.0192
2.0GPM 40	0.0909	0.1016	0.0107
1.5GPM 80	0.1060	0.0977	-0.0083
2.0GPM 80	0.1071	0.1571	0.0500

a. (C-A) means (center - average) volume per area

Pressure: 10 psi

Table 4.3 Evaluation of Speed Using a Control Box

Dial setting	6		7		8		9		10	
	Right	Left	Right	Left	Right	Left	Right	Left	Right	Left
1	22.32	21.22	19.41	18.53	17.78	17.28	16.88	16.53	16.87	16.34
2	22.09	21.32	19.18	18.53	17.75	17.09	16.91	16.13	16.78	16.03
3	21.94	20.75	19.28	18.72	17.75	16.84	17.07	16.13	17.04	16.59
4	22.31	21.28	19.22	18.56	17.81	17	16.97	16.84	16.91	16.34
5	21.62	20.94	19.16	18.62	17.75	17.13	17	16.78	17.06	16.54
6	22.09	21.22	19.34	18.54	17.9	17.06	17.09	16.78	16.91	16.78
Average	22.062	21.122	19.265	18.583	17.79	17.067	16.987	16.532	16.928	16.437
Std	0.2607	0.2258	0.0971	0.075	0.059	0.1456	0.0841	0.329	0.1057	0.2593
Speed (cm/sec)	4.0795	4.261	4.6717	4.843	5.059	5.2734	5.2983	5.4441	5.3165	5.4756

5.06 m/sec (Leonas et al., 1988). According to the standard test method of laboratory spray test for agricultural application (ASTM E 641-85), 40 psi was selected for spraying.

4.2 CALIBRATION CURVE (HPLC)

The calibration of the HPLC for atrazine response was determined using a series of atrazine standard solutions that contained a known quantity of the internal standard, simazine. Three samples of each of the eight standards of atrazine are analyzed by HPLC (Table 4.4). The HPLC-UV response for simazine, the internal standard, was constant throughout the study for all samples i.e., standards as well as unknowns. The HPLC-UV response i.e., area under the curve, was ratioed to the HPLC-UV response for simazine. This data is reported in a two-dimensional scatter plot with the ratio of atrazine to simazine response on the x-axis and atrazine concentration in the y-axis (Figure 4). This was determined to be a response for 10-100 ppm atrazine with a correlation coefficient (R^2) of 0.9761. The intercept was 7.1228 and the slope of the standard calibration curve was 41.8880 ($y = 41.8880\ x + 7.1228$), where x is the ratio of HPLC-UV response of atrazine to simazine and y is the atrazine concentration in the unknown samples. The concentration of atrazine was measured to microgram per milliliter in methanol.

4.3 INSTRUMENT SENSITIVITY

The balance was calibrated every day before testing. Chromatographic grade chemicals such as methanol, acetonitrile and deionized water were filtered every day before running the HPLC or GC analysis. The minimum detectability was less than 0.001 ppb and was 7 ppm for the HPLC.

4.4 MASS BALANCE

The mass balance was measured by the mass balance equation. The average speed of the mechanical movement from the left to the right was 4.809 (cm/sec). The flow rate was 8.94324 (ml/sec) at 40 psi. The angle from the Fan Spray® 1.5GPM40 nozzle tip was 45.24 ° and the width along the sample was 25.4 cm (10 in). The height from the end of the nozzle tip to the sample holder was at 30.48 cm (12 in). The theoretical concentration of atrazine and chlorpyrifos

Table 4.4 Standard Concentration of Atrazine

Conc. of Atrazine (μg/ml)	Atrazine (x 10^6 Peak Response)	Simazine (x 10^6 Peak Response)	Ratio (Atrazine/Simazine)
10	2.85	17.9	0.16
20	5.00	16.4	0.30
30	8.53	15.0	0.57
40	16.6	15.3	1.08
50	12.4	15.5	0.80
60	18.8	16.4	1.15
70	20.4	14.0	1.46
90	25.5	14.0	1.82
100	32.4	13.8	2.35
Average	15.8311	15.3667	1.0767
Standard Deviation	9.6772	1.3647	0.7162

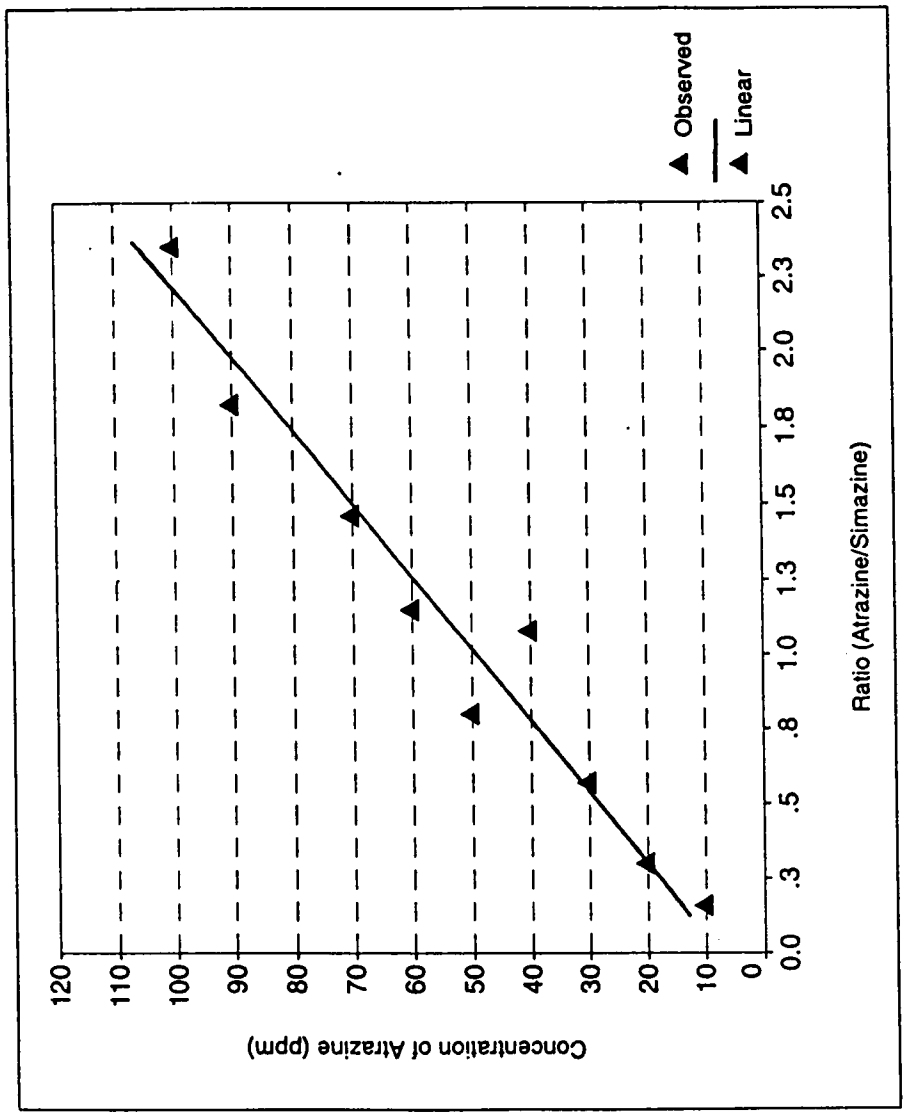


Figure 4 Standard Calibration Curve

applied to the center 25.81 cm^2 (4 in^2) was 1.8422 g for atrazine 2.5 % solution, and 1.7104 g forchlorpyrifos 1.0 % solution, and 0.0555 g for atrazine, 0.0171 g for chlorpyrifos respectively. A petri dish was used to measure the actual mass balance of atrazine 2.5 % and chlorpyrifos 1.0 % solutions that were sprayed on the samples in the 25.81 cm^2 (4 in^2) center area. The theoretical amount of chlorpyrifos showed similar results in both tests but atrazine did not. The mass balance applied on the 25.81 cm^2 (4 in^2) 1.57419 g when using distilled water, 2.233544 g, when using atrazine and 1.713544 g for chlorpyrifos. Due to the differences between the two test results, the petri-dish test data was chosen as the mass used to calculate the penetration efficiency of the pesticides. The amount of atrazine sprayed on the outside barrier fabric in the 25.81 cm^2 (4 in^2) were 1345 ppm and 343 ppm for chlorpyrifos.

4.5 SPIKE AND RECOVERY

To verify the extraction method for removing atrazine and chlorpyrifos from the cotton knit collecting fabric, the samples were spiked with 1 ml of 10 ppm atrazine standard solution and this was recovered using 50 ml methanol. The efficient of atrazine was 94.65% (Table 4.5)

- Theoretical concentration of atrazine:
  500 μg/ 51 ml methanol (1 ml + 50 ml) = 9.8039 ppm
- Atrazine concentration of spike test (calculated from the standard curve):
  0.1469/0.16 (ratio) x 10 ppm = 9.1813 ppm
- Percent extraction of atrazine:
  9.1813/9.8039 x 100 = 94.65 %

4.6 IMAGE ANALYSIS

Image analysis was used to determine the fabric characteristics of nonwoven materials: fiber and pore diameters of the spunbond nonwoven layer and web uniformity of nonwoven fabrics. Even though measurement was limited to only a thin layer, it gave some useful idea about penetration as related to the nonwoven layer under the coating or lamination material. Especially, web uniformity correlated with the penetration efficiency.

Table 4.5 Spike Test of Atrazine

Average of Three Replicates	Atrazine ($x10^6$ Peak Response)	Simazine ($x10^6$ Peak Response)	Ratio (Atrazine/Simazine)
1	2.51	17.1	0.1468
2	2.59	16.9	0.1533
3	2.46	16.9	0.1456
4	2.46	17.3	0.1422
5	2.41	16.4	0.1470
Average	2.486	16.92	0.1469
Standard Deviation	0.0680	0.3347	0.0040

4.6 1 Fiber Diameter

Fiber diameters of each spunbond layer of the SMS (SMS-S), MSB, CSB, meltblown layer of the (SMS-M) and Tyvek® was measured by using optical microscopy. Fiber diameter of SMS-M varied a lot due to the characteristics of the meltblown process, which is more affected by the air flow than the spunbond process. The fiber diameter of Tyvek® also varied because the fiber diameter was stretched when the material was separated into layers. The mean value of fiber diameter was 19.29 μm for SMS, 22.1 μm for MSB and 19.75 μm for CSB spunbond layers. Individual fiber diameter of the spunbond layer (SMS-S) in SMS and CSB fabric had a similar value. While the coefficient of variation of SMS spunbond was smaller than that of CSB, the SMS spunbond layer had more uniform diameter distribution of fiber and smaller diameter than CSB. The mean fiber diameter of the MSB spunbond layer was larger than those of the others and the coefficient of variation was larger than others (8.4 percent). Therefore, the MSB spunbond layer had more variations in fiber diameter and the average diameter was larger than others.

4.6.2 Pore Diameter

The pore diameter of the MSB and CSB spunbond layers is shown in Table 4.6 and pore images are shown in Figure 5. The mean pore size of the MSB spunbond layer was 25.9 μm and that of the CSB was 28.1μm, which indicated that the MSB had smaller pores than that of the CSB. There were total of 3,820 pores in the spunbond layer of MSB and 4,578 pores in the spunbond layer of CSB. Figure 6 shows that the bonding area of MSB was darker than other parts and had fewer pores in it while CSB showed no bonding area. Figure also shows that fibers in the MSB spunbond layer were packed closer than those fibers in the CSB spunbond layer. The percent of pore area in MSB was 9.5 and CSB had 13.4, which also meant that MSB had better fiber packing.

4.6.3 Fiber Web Uniformity

Web uniformity of SMS, MSB, CSB and Tyvek® are shown in Table 4.6 and the images of those fabrics are shown in Figure 6. Each fabric had smaller coefficient of variation value for machine direction than cross direction, which indicated that the fiber of machine direction was elongated than that of the cross direction.

Table 4.6. Image Analysis of Fabric

Spunbond Diameter (μm)	Fabric Type	Number of Fiber	Mean (μm)	CV (%)	Min (μm)	Max (μm)
	SMS-S	30	19.29	4.68	17.55	20.79
	SMS-M	30	5.86	40.9	3.2	10.19
	MSB-S	50	22.10	8.40	18.00	26.40
	CSB-S	30	19.75	6.53	16.33	21.98
	Tyvek®	25	6.92	33.9	3.04	12.51

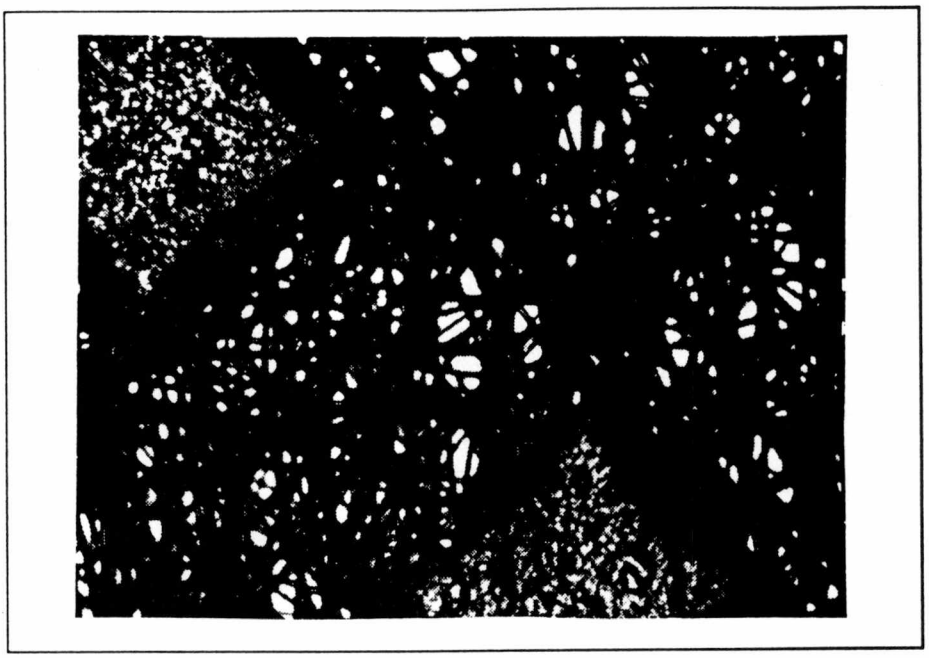
Spunbond Pore Diameter (μm)	Fabric Type	Mean (μm)	CV (%)	Min (μm)	Max (μm)	No. of Pores	No. of Pores /Area (mm^2)	Cover (%)
	MSB-S	25.9	69.1	7.4	197.6	3820	114.9	9.50
	CSB-S	28.1	69.4	7.4	194.3	4578	137.7	13.4

Web Uniformity of Fabric	Fabric Type	Wt (g/m^2) or (gray L)	Direction (CD or MD)	Min CV (%)	Max CV (%)
	SMS	118	CD	3.3	45
			MD	2.8	44.7
			Total	3.7	45.7
	MSB	91.6	CD	0.8	19.7
			MD	1.7	17.9
			Total	1.8	19.9
	CSB	109.8	CD	3.3	8.1
			MD	2.9	7.6
			Total	3.7	8.6
	Tyvek®	103.7	CD	9.4	34.6
			MD	9	34.9
			Total	10.3	37.1

S indicates spunbond

M indicates meltblown

MSB



CSB

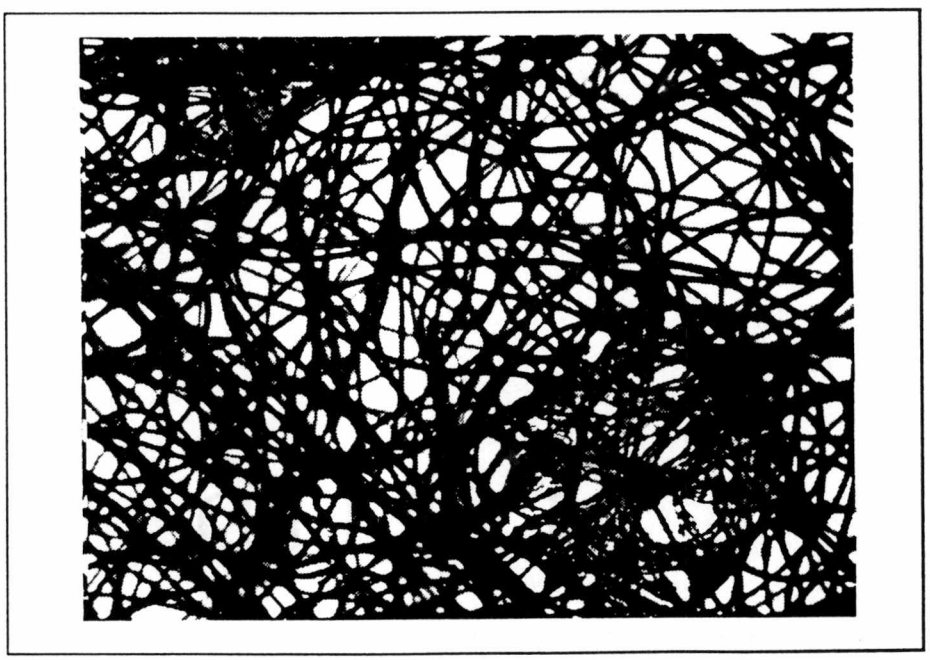
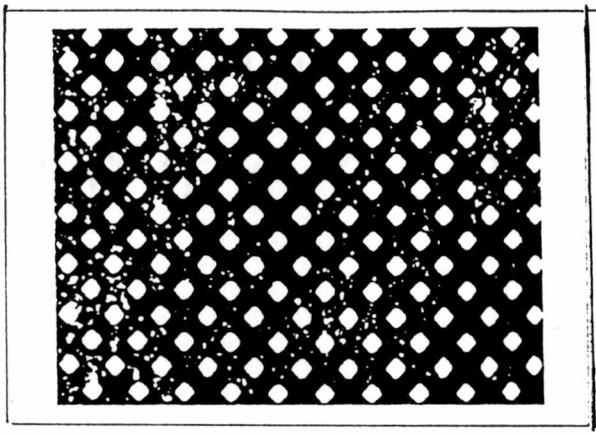
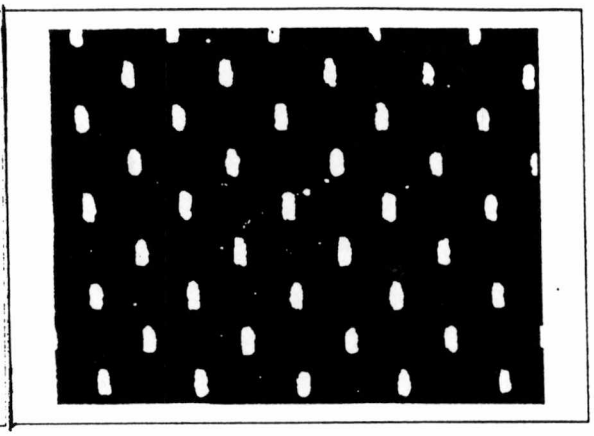


Figure 5 Pore Image of Spunbond Layer

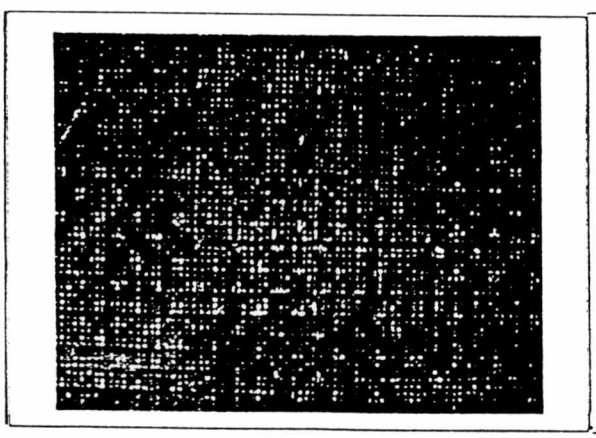
SMS



MSB



CSB



Tyvek®1422

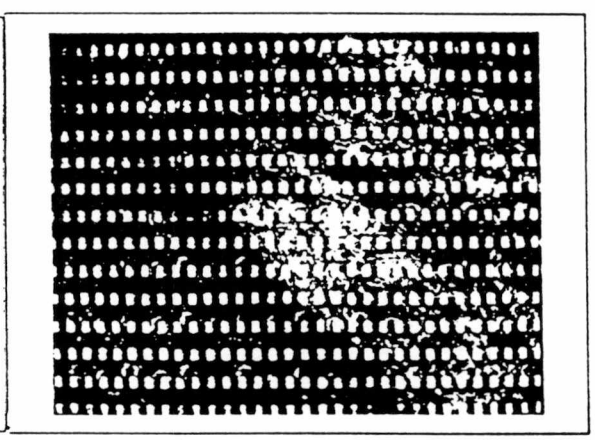


Figure 6 Web Image of Nonwoven Fabric

SMS had coefficient of variations of a ranging from a minimum of 3.7 to a maximum of 45.7 while for MSB minimum value was 1.8 and maximum value was 19.9. CSB had coefficient of variations from 3.7 to 8.6 while Tyvek® had values from 10.3 to 37.1. CSB had the smallest range of coefficient of variation indicating that web uniformity of CSB was better than that of other fabrics. MSB had a smaller range than SMS and Tyvek®, indicating better web uniformity. Figure 6 shows that gray levels varied in Tyvek® and SMS fabrics. Especially, in case of Tyvek®, a dark thick stripe on the left side of the figure indicated a big fiber bundle. Tyvek® had a smaller range of coefficient of variation than SMS indicating that Tyvek® had more uniform web structure than that of SMS. Measuring the web uniformity using original fabrics prevented any fiber deformation or distortion from separation of the spunbond layer, and hence allowed fabric characteristics to be compared. The variation of web uniformity in CSB and MSB was about 10 to 20 percent. The variation of web uniformity in SMS and Tyvek® was about 40 percent. Image analysis showed that CSB had the most uniform web structure and MSB had the second best uniform web structure. Next was Tyvek® and SMS was the last. Pore diameter indicated that the spunbond layer of MSB had less pore area than that of CSB. Despite the larger pore area in the spunbond layer, CSB had more uniform web than MSB. Image analysis of fiber diameter showed that the spunbond layers of SMS, MSB and CSB were not significantly different. However, CSB had smaller and more uniform diameters than MSB, which is related to the better web uniformity of CSB.

4.7 ANALYSIS OF PESTICIDE PENETRATION

Penetration of atrazine and chlorpyrifos with weight and without weight were analyzed using a GC and a HPLC. The penetration of atrazine with and without weight (2psi, 1min) determined using a GC and a HPLC is shown in Table 4.7, and the penetration of chlorpyrifos with and without weight (2 psi. 1min) determined using GC is shown in Table 4.8. Barrier efficiencies of pesticides are shown in Table 4.9-4.11. A general linear model (GLM) of chlorpyrifos penetration (ppm) separated by weight application is shown in Table 4.12 and separated by grouping variables of fabric type and weight application is shown in Table 4.13. GLM tests were performed excluding SMS fabric to make the data of chlorpyrifos penetration was normally distributed. Test statistics of without weighted chlorpyrifos penetrations were 100577.47 for sum

Table 4.7 Penetration (ppm) of Atrazine Without and With Weight (2psi) Determined Using GC and HPLC Data

Analytical Method	Pressure Application	Fabric Type	Count	Mean (ppm)	Std Deviation	Std Err of Mean
GC	No Weight	SMS	6	92.90	22.02	9.85
		MSB	6	15.73	10.82	4.42
		CSB	6	21.10	16.32	6.66
		Tyvek®	6	30.15	13.17	5.38
		Cotton	6	419.87	41.73	17.04
		Denim	6	54.93	11.39	4.65
	Weight (2psi)	SMS	2	67.70	13.29	9.40
		MSB	2	10.75	4.17	2.95
		CSB	2	14.55	12.37	8.75
		Tyvek®	2	16.30	10.47	7.40
		Cotton	2	429.95	77.85	55.05
		Denim	2	125.30	9.48	6.70
HPLC	No Weight	SMS	9	93.60	14.25	4.75
		MSB	9	25.88	8.43	2.81
		CSB	9	35.89	14.98	4.99
		Tyvek®	9	35.23	12.77	4.26
		Cotton	9	477.50	2.94	0.98
		Denim	9	53.01	3.55	1.18
	Weight (2psi)	SMS	3	74.28	1.28	0.74
		MSB	3	14.38	0.48	0.28
		CSB	3	12.43	0.24	0.14
		Tyvek®	3	17.18	0.42	0.24
		Cotton	3	312.49	10.66	7.54
		Denim	3	135.02	14.27	8.24

Table 4.8 Penetration (ppm) of Chlorpyrifos Without and With Weight (2psi) Determined Using GC Data

Analytical Method	Pressure Application	Fabric Type	Count	Mean (ppm)	Std Deviation	Std Err of Mean
GC	No Weight	SMS	6	154.17	65.93	26.92
		MSB	6	8.00	3.58	1.46
		CSB	6	7.67	3.27	1.33
		Tyvek®	6	19.33	9.81	4.01
		Cotton	6	153.50	16.28	6.65
		Denim	6	91.67	12.88	5.26
	Weight (2psi)	SMS	2	130.00	.	.
		MSB	2	6.50	3.54	2.50
		CSB	2	3.00	1.41	1.00
		Tyvek®	2	71.00	12.73	9.00
		Cotton	2	116.50	4.95	3.50
		Denim	2	105.00	9.90	7.00

Table 4.9 Barrier Efficiency of Atrazine Without and With Weight (2psi) Determined Using GC Data

	Cotton Fabric under Protective Fabric	Conc. (ppm)	Conc. of Atrazine (mg/cm^2)	Percent Penetration (%)	Barrier Efficiency (%)
No Weight	SMS	93	0.1802	6.9	93.1
	MSB	16	0.0310	1.2	98.8
	CSB	21	0.0407	1.6	98.4
	Tyvek®	30	0.0581	2.2	97.8
	Cotton	420	0.8138	31.2	68.8
	Denim	55	0.1066	4.1	95.9
Weight (2psi)	SMS	68	0.1318	5.1	94.9
	MSB	11	0.1213	0.8	99.2
	CSB	15	0.0291	1.1	98.9
	Tyvek®	16	0.0310	1.2	98.8
	Cotton	430	0.8331	32.0	68.0
	Denim	125	0.2422	9.3	90.7

Table 4.10 Barrier Efficiency of Chlorpyrifos Without and With Weight (2psi) Determined Using GC Data

	Cotton Fabric under Protective Fabric	Conc. (ppm)	Conc. of Chlorpyrifos (mg/cm^2)	Percent Penetration (%)	Barrier Efficiency (%)
No Weight	SMS	154	0.2984	44.9	55.1
	MSB	8	0.0155	2.3	97.7
	CSB	8	0.0155	2.3	97.7
	Tyvek®	19	0.0368	5.5	94.5
	Cotton	154	0.2984	44.9	55.1
	Denim	92	0.1783	26.8	73.2
Weight (2psi)	SMS	130	0.2519	37.9	62.1
	MSB	7	0.0136	2.0	98.0
	CSB	3	0.0058	0.9	99.1
	Tyvek®	71	0.1376	20.7	79.3
	Cotton	117	0.2267	34.1	65.9
	Denim	105	0.2034	30.6	69.4

Table 4.11 Barrier Efficiency of Atrazine Without and With Weight (2psi) Determined Using HPLC Data

	Cotton Fabric under Protective Fabric	Conc. (ppm)	Conc. of Atrazine (mg/cm^2)	Percent Penetration (%)	Barrier Efficiency (%)
No Weight	SMS	94	0.1821	7.0	93.0
	MSB	26	0.0504	1.9	98.1
	CSB	36	0.0698	2.7	97.3
	Tyvek®	35	0.0678	2.6	97.4
	Cotton	478	0.9261	35.5	64.5
	Denim	53	0.1027	3.9	96.1
Weight (2psi)	SMS	74	0.1434	5.5	94.5
	MSB	14	0.0271	1.0	99.0
	CSB	12	0.0233	0.9	99.1
	Tyvek®	17	0.0329	1.3	98.7
	Cotton	312	0.6045	23.2	76.8
	Denim	135	0.2616	10.0	90.0

Table 4.12 General Linear Model of Chlorpyrifos Penetration (ppm) Separated by Weight

Weight	Source	Sum of Squares	df	Mean Square	F	Sig.	Observed Power[a]
No Weight	Corrected Model	100577.47[b]	4	25144.367	228.295	.000	1.000
	Intercept	94192.033	1	94192.033	855.203	.000	1.000
	Fabric[d]	100577.47	4	25144.367	228.295	.000	1.000
	Error	2753.500	25	110.140			
	Total	197523.00	30				
	Corrected Total	103330.97	29				
Weight (2psi)	Corrected Model	22897.400[c]	4		95.725	.000	1.000
	Intercept	36481.600	1	5724.350	610.060	.000	1.000
	Fabric	22897.400	4	36481.600	95.725	.000	1.000
	Error	299.000	5	5724.350			
	Total	59678.000	10	59.800			
	Corrected Total	23196.400	9				

a. Computed using alpha = .05

b. R Square = .973 (Adjusted R Squared = .969)

c. R Square = .987 (Adjusted R Squared = .977)

d. Fabric SMS excluded

Table 4.13 General Linear Model of Chlorpyrifos Penetration (ppm) Separated by Weight and Fabric

Source	Sum of Squares	df	Mean Square	F	Sig.	Observed Power[a]
Corrected Model	123617.88[b]	9	13735.319	134.991	.000	1.000
Intercept	101675.41	1	101675.41	999.267	.000	1.000
Weight	143.008	1	143.008	1.405	.245	.209
Fabric[c]	78417.467	4	19604.367	192.672	.000	1.000
Weight*Fabric	6217.367	4	1554.342	15.276	.000	1.000
Error	3052.500	30	101.750			
Total	257201.00	40				
Corrected Total	126670.38	39				

a. Computed using alpha = .05

b. R Square = .976 (Adjusted R Squared = .969)

c. Fabric SMS excluded

of squares, 4 for degree of freedom, and 25144.367 for the mean square. The p-value showed the mean value was significantly different when separated by fabric type at 95 % confidence interval (Table 4.12). Test statistics of weighted chlorpyrifos penetrations were 22897.400 for sum of squares, 4 for degree of freedom, and 36481.600 for the mean square. The p-value showed the mean value was significantly different (at 95 % confidence interval) when separated by weight and fabric type (Table 4.13). Test statistics of chlorpyrifos penetrations separated by weight application type were 143.008 for sum of squares, 1 for degree of freedom, and 143.008 for the mean square. P-value showed the mean value for weight was not significantly different at 95 % confidence interval (Table 4.13). Test statistics of chlorpyrifos penetrations separated by fabric type were 78417.467 for sum of squares, 4 for degree of freedom, and 19604.367 for the mean square. The p-value showed the mean value for fabric type was significantly different at 95 % confident interval (Table 4.13). Test statistics of chlorpyrifos penetrations separated by weight application type and fabric type were 6217.367 for sum of squares, 4 for degree of freedom, and 1554.342 for the mean square. P-value showed the mean value for weight*fabric was significantly different at 95 % confidence interval (Table 4.13). Non parametric tests of chlorpyrifos were compared to the results of GLM separated by fabric type and weight application (Table 4.14). Non parametric rank tests included SMS. The value of the Wilcoxon test by using a grouping variable of weight application was 244.000 and the p-value indicated that there was no significant difference between whether weight was applied or not. The Kruskal-Wallis test was performed to analyze more than two variables such as fabric types. Test staticstic of chi-square was 39.583, degree of freedom was 5 and the p-value (2-tailed) indicated that there was significant difference at the 95 % confidence interval. The order of increasing rank was CSB, MSB, Tyvek®, SMS, denim and cotton. CSB and MSB had a similar rank; these fabrics had the smallest penetration and the best barrier efficiency against chlorpyrifos. SMS and cotton had the similar highest rank; these fabrics had the largest penetration and the least barrier efficiency. Non parametric tests of atrazine penetration (ppm) separated by fabric type, weight application and analysis type are shown in Table 4.15. The value of the Wilcoxon test by using a grouping variable of analytical method was 2623.000 and the p-value (2-tailed) indicated that there was no significant difference between GC or HPLC. Test statistic of the Wilcoxon test by using a grouping variable of weight application was 1521.500 and p-value (2-tailed) indicated that there was no significant difference at 95 % confidence interval. The Kruskal Wallis test was performed to analyze by fabric type. The value of the chi-square was 95.040, degree of freedom was 5 and

Table 4.14 Non-Parametric Tests of Chlorpyrifos Penetration (ppm) Using by Different Grouping Variables

Grouping Variable : Weight Application				
		N	Mean Rank	Sum of Ranks
Ranks	No. Weight	36	24.56	884.00
	Weight (2psi)	11	22.18	244.00
	Total	47		
	Mann-Whitney U	Wilcoxon W	Z	Asymp. Sig. (2- tailed)
Test Statistics	178.000	244.000	-.503	.615

Grouping Variable : Fabric Type				
		N	Mean Rank	
Ranks	SMS	7	38.14	
	MSB	8	10.00	
	CSB	8	8.38	
	Tyvek®	8	19.25	
	Cotton	8	40.00	
	Denim	8	30.00	
	Total	47		
Test Statistics	Chi-Square	df		Asymp. Sig. (2- tailed)
(Kruskal Wallis Test)	39.583	5		.000

Chlorpyrifos penetration through the fabrics with and without weight were not significant at the p = 0.05 using the Non-Parametric test, Mann-Whitney Unuvariable.

Table 4.15 Non-Parametric Tests of Atrazine Penetration (ppm) Using by Different Grouping Variables

Grouping Variable : Analysis Type				
		N	Mean Rank	Sum of Ranks
Ranks	GC	47	55.81	2623.00
	HPLC	71	61.94	4398.00
	Total	118		
	Mann-Whitney U	Wilcoxon W	Z	Asymp. Sig. (2- tailed)
Test Statistics	1495.000	2623.000	-.954	.340
Grouping Variable : Weight application				
		N	Mean Rank	Sum of Ranks
Ranks	No. Weight	89	61.79	5499.50
	Weight (2psi)	29	52.47	1521.50
	Total	118		
	Mann-Whitney U	Wilcoxon W	Z	Asymp. Sig. (2- tailed)
Test Statistics	1086.500	1521.500	-1.275	.202
Grouping Variable : Fabric Type				
		N	Mean Rank	
Ranks	SMS	19	84.89	
	MSB	20	24.98	
	CSB	20	30.85	
	Tyvek®	20	38.55	
	Cotton	19	109.00	
	Denim	20	72.47	
	Total	118		
Test Statistics	Chi-Square	df		Asymp. Sig. (2- tailed)
(Kruskal Wallis Test)	95.040	5		.000

the p-value (2-tailed) indicated that there was significant difference by fabric type at the 95 % confidence interval. The order of increasing rank was MSB, CSB, Tyvek®, denim, SMS and cotton. MSB and CSB had the smallest penetration and the best barrier efficiency. Cotton had the greatest penetration and the least barrier efficiency against atrazine. The results of statistical analysis using grouping variables showed that there was significant difference among fabric types and there was no significant difference between the analysis method and weight applications in both atrazine and chlorpyrifos penetrations. Based on Levene's test for equal variances, a t-test was conducted for data having equal variances to analyze the level of mean difference between two independent variables. A non-parametric test was conducted for data having unequal variances of two independent variables.

4.7.1 Gas Chromatography

The amount of pesticide penetration was calculated to milligram per centimeter squared. The total amount of atrazine was 2.6056 and of chlorpyrifos was 0.6646 milligram per centimeter squared (mg/cm^2). Percent penetration was calculated based on the total amount of pesticide applied. Barrier efficiency was reported as the opposite term of percent penetration.

4.7.1.1 Atrazine Without Weight

Except for cotton, the fabrics tested showed a good protection, above 93 percent against atrazine penetration (Table 4.9). MSB showed the best barrier efficiency, 98.8 percent, which was similar to that of CSB and Tyvek®. Tyvek® had a little less barrier efficiency than MSB and CSB but still showed a good protection. Blue denim, whose barrier efficiency was 95.9, showed a little less than MSB, CSB and Tyvek®, but about 3 percent better than SMS.

4.7.1.2. Atrazine With Weight

The penetration of atrazine with weight, which was applied for one minute is shown in the Table 4.9. Data of pressure application showed that the penetration of atrazine was similar to that of atrazine without weight. MSB, CSB and Tyvek® showed similar penetration and SMS showed a little less but still good protection when pressure was applied. Percent penetration of blue denim was 9.3 percent and cotton was 32.0 percent. Blue denim provided much better protection than cotton but eight times more penetration by atrazine than MSB, CSB and Tyvek®, and twice that of SMS. Figure 7 shows the penetration of atrazine with and without weight test using data analyzed with a GC. To compare the penetration the without and with weight, nonwovens showed a little

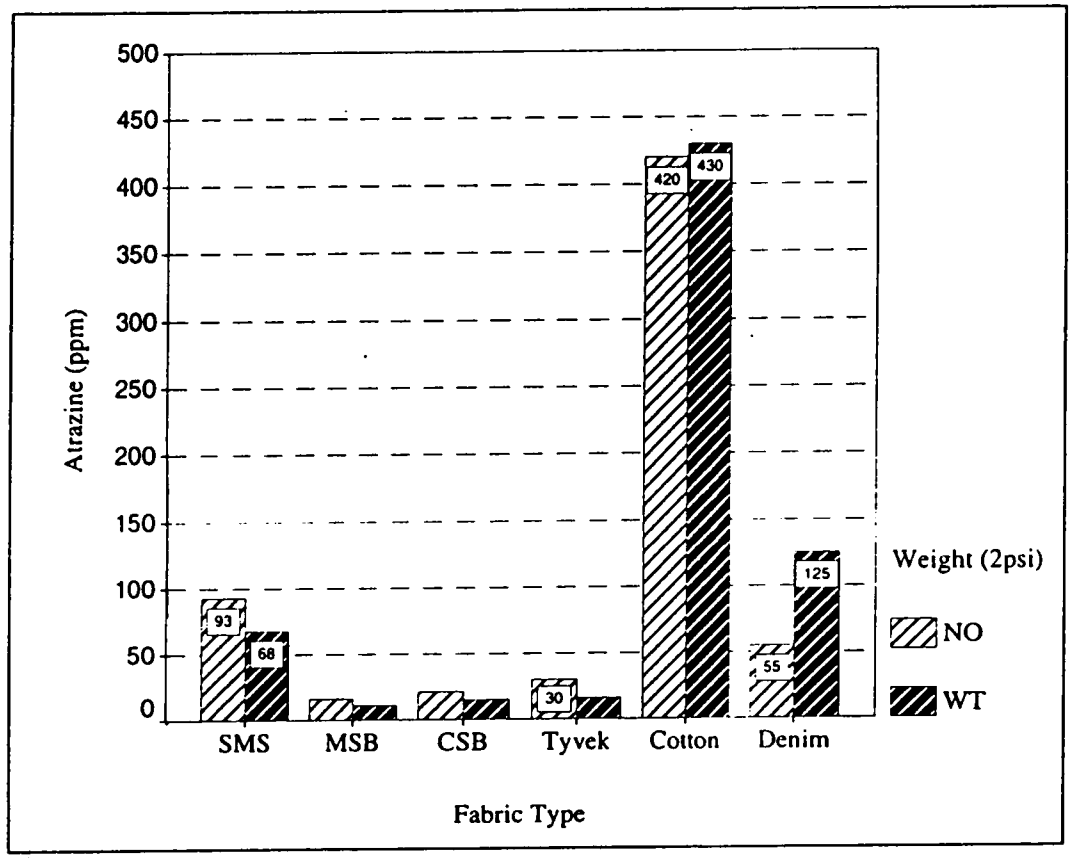


Figure 7 Atrazine Penetration With and Without Weight Determined Using GC Data

increased penetration when pressure was applied while cotton and blue denim showed increased penetration. Especially, the percent of penetration of blue denim increased twice when weight was applied while cotton showed similar larger penetration. Levene's test for equal variances showed that penetration data of atrazine both without weight and with weight had equal variances, so a t-test was preferred to a non-parametric test to analyze the difference of mean value. Test statistics of denim in terms of penetration was –7.771 for t-value and 6 for degree of freedom. P-value showed the mean value of denim was significantly different when the weight was applied compared to no weight at 95 % confidence interval (Table 4.16). The other fabrics were not significantly different whether the weight was applied or not. The Mann-Whitney non-parametric test supported the same results (Table 4.17). Test statistic of the Wilcoxon test by using a grouping variable of weight application of denim in terms of atrazine penetration was 21.000 and the p-value indicated that there was significant different at 95 % confidence interval. The other fabrics were not significantly different whether the weight was applied or not.

4.7.1.3 Chlorpyrifos Without Weight

MSB and CSB show a similar protection against chlorpyrifos and the percent penetration of Tyvek® was twice as great as MSB and CSB but it still provided good protection (Table 4.10). Barrier efficiencies of MSB, CSB and Tyvek® were above 94 percent. Percent penetration of blue denim was 26.8, and cotton and SMS allowed the same percent penetration, about 45 percent. SMS nonwoven provided bad protection against chlorpyrifos, allowing more than 40 percent penetration. Blue denim showed five times more penetration (%) of chlorpyrifos than atrazine indicating that it is not appropriate for agricultural protective clothing when liquid chlorpyrifos is sprayed in field applications.

4.7.1.4 Chlorpyrifos With Weight

Percent penetration of SMS was 37.9 percent, which was even greater than that of cotton and denim. SMS provided the worst protection against chlorpyrifos when weight was applied.
In conclusion; cotton, blue denim, and SMS are not good choices for agricultural apparel during chlorpyrifos application. MSB and CSB provided excellent protection against chlorpyrifos in both without and with weight tests. Tyvek® provided good protection but the protection was sensitive to the application of external pressure. Figure 8 shows the chlorpyrifos penetration with and without weight determined using a GC. Levene's test for equal variances showed that penetration data of atrazine for both without weight and with weight had equal variances;

Table 4.16 T-Test of Atrazine (ppm) between Without and With Weight Using GC Data

Levene's Test		T-test for Equality of Means						
		F	Sig.	t	df	Sig. (2 -tailed)	Mean Difference	Std. Error Difference
SMS	Equal variances assumed	.706	.439	1.464	5	.203	25.2000	17.2148
	Equal variances not assumed			1.851	3.382	.151	25.20000	13.6148
MSB	Equal variances assumed	1.283	.301	.609	6	.565	4.9833	8.1838
	Equal variances not assumed			.938	5.242	.389	4.9833	5.3118
CSB	Equal variances assumed	.051	.829	.510	6	.628	6.5500	12.8451
	Equal variances not assumed			.596	2.339	.604	6.5500	10.9981
Tyvek®	Equal variances assumed	.077	.790	1.330	6	.232	13.85..	10.4157
	Equal variances not assumed			1.514	2.211	.258	13.8500	9.1463
Cotton	Equal variances assumed	1.958	.211	-.249	6	.812	-10.0833	40.5063
	Equal variances not assumed			-.175	1.198	.886	-10.0833	57.6255
Denim	Equal variances assumed	.084	.781	-7.771	6	.000	-70.3667	9.0552
	Equal variances not assumed			-8.692	2.097	.011	-70.3667	8.1545

Table 4.17 Mann-Whitney Test of Atrazine penetration (ppm) between Without and With Weight Using GC Data

Fabric Type	Case	N	Mean Rank	Sum of Ranks
SMS	No. Weight	5	4.60	23.00
	Weight (2psi)	2	2.50	5.00
	Total	7		
MSB	No. Weight	6	4.83	29.00
	Weight (2psi)	2	3.50	7.00
	Total	8		
CSB	No. Weight	6	4.50	27.00
	Weight (2psi)	2	4.50	9.00
	Total	8		
Tyvek®	No. Weight	6	5.33	32.00
	Weight (2psi)	2	2.00	4.00
	Total	8		
Cotton	No. Weight	6	4.33	26.00
	Weight (2psi)	2	5.00	10.00
	Total	8		
Denim	No. Weight	6	3.50	21.00
	Weight (2psi)	2	7.50	15.00
	Total	8		

Test Statistics[c]			SMS	MSB	CSB	Tyvek®	Cotton	Denim
Mann-Whitney U			2.000	4.000	6.000	1.000	5.000	.000
Wilcoxon W			5.000	7.000	9.000	4.000	26.000	21.000
Z			-1.162	-.667	.000	-1.667	-.333	-2.000
Asymp. Sig. (2-tailed)			.245	.505	1.000	.096	.739	.046
Exact Sig.[2*(1-tailed Sig.)]			.381[a]	.643[a]	1.000[a]	.143[a]	.857[a]	.071[a]
Monte Carlo Sig. (2-tailed)	Sig.		.378[b]	.636[b]	1.000[b]	.141[b]	.854[b]	.069[b]
	99% Confidence	Lower Bound	.391	.623	1.000	.132	.845	.062
		Upper Bound	.190[b]	.648[b]	1.000[b]	.150[b]	.863[b]	.076[b]
Monte Carlo Sig. (1-tailed)	Sig.		.180	.324	.578	.071	.422	.035
	99% Confidence	Lower Bound	.200	.311	.566	.064	.409	.030
		Upper Bound		.336	.591	.077	.434	.040

a. Not corrected for ties

b. Based on 10000 sampled tables with starting seed 2000000

c. Grouping Variable: CASE

d. Denim different from all others and all others not different

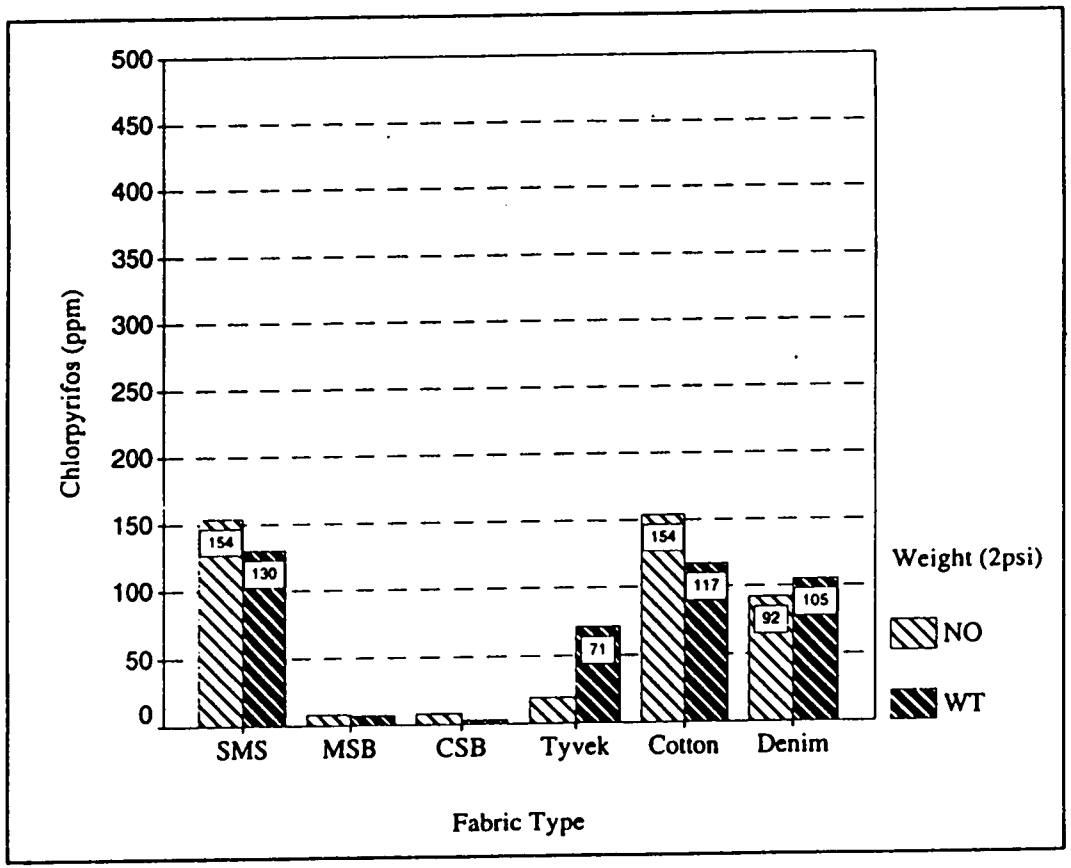


Figure 8 Chlorpyrifos Penetration With and Without Weight Determined Using GC Data

therefore, a t-test was preferred to a non-parametric test to analyze the difference of mean value. Test statistics of cotton in terms of penetration were 3.021 for t-value, 6 for degree of freedom, 37.000 ppm for mean difference and 12.2474 ppm for standard error difference. P-value showed the mean value of cotton and Tyvek® were significantly different when the weight was applied at 95 % confidence interval (Table 4.18). The other fabrics were not significantly different whether weight was applied or not. The Mann-Whitney non-parametric test supported similar results (Table 4.19). For Tyvek® test statistic of the Wilcoxon test by using a grouping variable of weight application was 21.000 and the p-value indicated that there was significant different at 95% confidence interval. For cotton, the test statistic of the Wilcoxon test by using a grouping variable of weight application was 3.000 and the p-value indicated that there was significant difference at 95% confidence interval. The other fabrics were not significantly different whether weight was applied or not.

4.7.2 High Performance Liquid Chromatography

Only atrazine was analyzed using a HPLC.

4.7.2.1 Atrazine Without Weight

Except for cotton, the fabrics tested showed good protection above 93 percent, against atrazine penetration, which were similar results using a GC (Table 4.11). MSB showed the best barrier efficiency, 98.1 percent, which was similar to CSB and Tyvek®,which had a similar barrier efficiency, about 97 percent, and a little bit less than MSB but still good protection. Blue denim provided a little less protection than MSB, CSB and Tyvek®, with 96.1 percent barrier efficiency, but was twice as effective against atrazine penetration as SMS.

4.7.2.2. Atrazine With Weight

Data of pressure application showed that the penetration of atrazine was similar to that without weight (Table 4.11). MSB, CSB and Tyvek® showed similar penetration and SMS showed a little less but still good protection when pressure was applied. Percent penetration of blue denim was 10.0 percent and cotton was 23.2 percent. Blue denim provided twice as good protection as cotton but allowed eight times more atrazine to penetrate compared to MSB, CSB and Tyvek®, and two times more than SMS. Figure 9 shows atrazine penetration with and without weight determined using a HPLC. To compare the penetration between the without and with weight, nonwovens and cotton showed a little decreased penetration with weight while blue

Table 4.18 T-Test of Chlorpyrifos (ppm) between Without and With Weight Using GC Data

Levene's Test		T-test for Equality of Means						
		F	Sig.	t	df	Sig. (2 -tailed)	Mean Difference	Std. Error Difference
SMS	Equal variances assumed	.	.	.339	5	.748	24.1667	71.2109
	Equal variances not assumed			.	.	.	24.1667	.
MSB	Equal variances assumed	.012	.917	.514	6	.625	1.5000	2.9155
	Equal variances not assumed			.518	1.758	.662	1.5000	2.8954
CSB	Equal variances assumed	1.074	.340	1.882	6	.109	4.6667	2.4795
	Equal variances not assumed			2.800	4.728	.040	4.6667	1.6667
Tyvek®	Equal variances assumed	.033	.863	-6.111	6	.001	-51.6667	8.4547
	Equal variances not assumed			-5.245	1.424	.067	-51.6667	9.8511
Cotton	Equal variances assumed	2.084	.199	3.021	6	.023	37.0000	12.2474
	Equal variances not assumed			4.925	5.892	.003	37.0000	7.5122
Denim	Equal variances assumed	.353	.574	-1.314	6	.237	-13.3333	10.1507
	Equal variances not assumed			-1.523	2.300	.251	-13.3333	8.7547

Table 4.19 Mann-Whitney Test of Chlorpyrifos Penetration (ppm) between Without and With Weight Using GC Data

Fabric Type	Case	N	Mean Rank	Sum of Ranks
SMS	No. Weight	6	4.17	25.00
	Weight (2psi)	1	3.00	3.00
	Total	7		
MSB	No. Weight	6	4.67	28.00
	Weight (2psi)	2	4.00	8.00
	Total	8		
CSB	No. Weight	6	5.33	32.00
	Weight (2psi)	2	2.00	4.00
	Total	8		
Tyvek®	No. Weight	6	3.50	21.00
	Weight (2psi)	2	7.50	15.00
	Total	8		
Cotton	No. Weight	6	5.50	33.00
	Weight (2psi)	2	1.50	3.00
	Total	8		
Denim	No. Weight	6	3.83	23.00
	Weight (2psi)	2	6.50	13.00
	Total	8		

Test Statistics[c]			SMS	MSB	CSB	Tyvek®	Cotton	Denim
Mann-Whitney U			2.000	5.000	1.000	.000	.000	2.000
Wilcoxon W			3.000	8.000	4.000	21.000	3.000	23.000
Z			-.500	-.333	-1.677	-2.012	-2.000	-1.333
Asymp. Sig. (2-tailed)			.617	.739	.094	.044	.046	.182
Exact Sig.[2*(1-tailed Sig.)]			.857[a]	.857[a]	.143[a]	.071[a]	.071[a]	.286[a]
Monte Carlo Sig. (2-tailed)	Sig.		.855[b]	.850[b]	.108[b]	.075[b]	.072[b]	.280[b]
	99% Confidence	Lower Bound	.846	.841	.100	.068	.065	.268
		Upper Bound	.864	.860	.115	.081	.078	.291
Monte Carlo Sig. (1-tailed)	Sig.		.425[b]	.428[b]	.068[b]	.040[b]	.038[b]	.140[b]
	99% Confidence	Lower Bound	.412	.415	.061	.035	.033	.131
		Upper Bound	.438	.441	.074	.045	.043	.149

a. Not corrected for ties

b. Based on 10000 sampled tables with starting seed 1238861123

c. Grouping Variable: CASE

d. Tyvek® and cotton different by weight chlorpyrifos GC

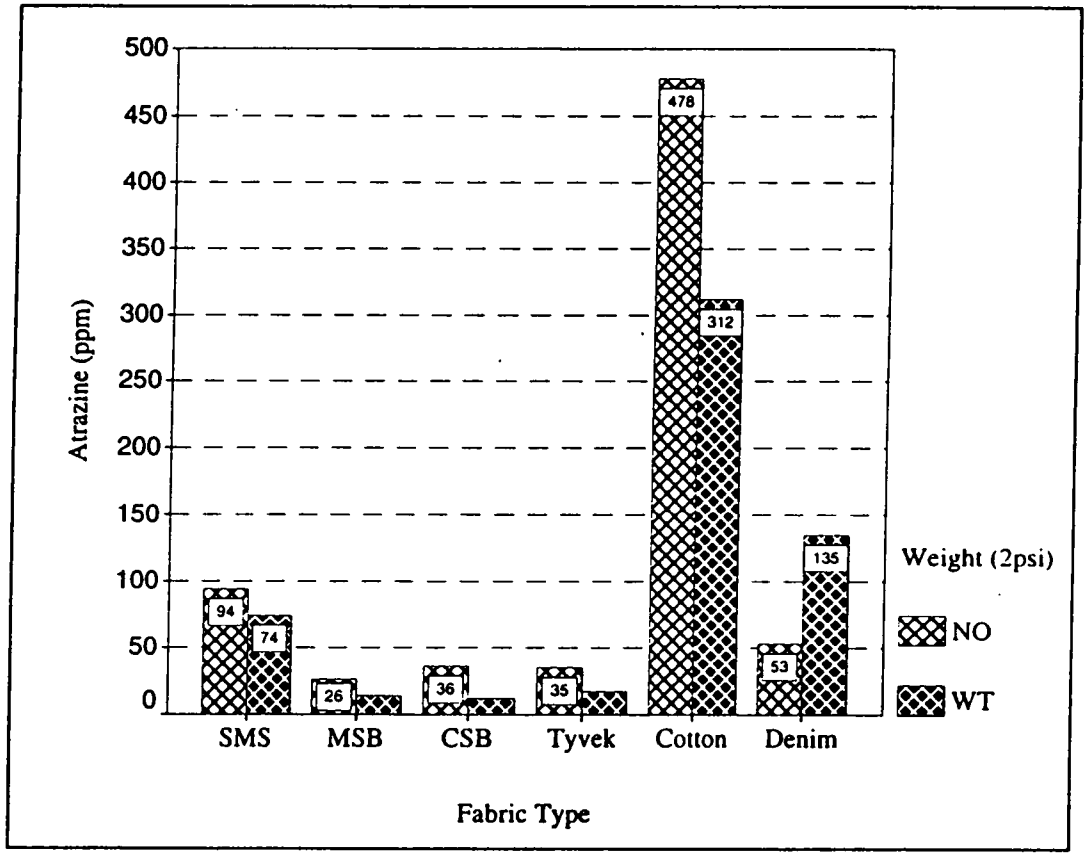


Figure 9 Atrazine Penetration With and Without Weight Determined Using HPLC Data

denim showed increased penetration when pressure was applied. Percent penetration of blue denim increased twice as much when weight was applied. Levene's test for equal variances showed that SMS, MSB, CSB, Tyvek® and denim did not have equal variances and cotton did. A non-parametric test was preferred to a t-test to analyze the difference of mean rank. Test statistics of SMS were 4.017 for t-value, 8.371 for degree of freedom, 19.3144 ppm for mean difference and 4.8084 ppm for standard error difference (Table 4.20). Test statistics of MSB were 4.074 for t-value, 8.157 for degree of freedom, 11.5000 ppm for mean difference and 2.8231 ppm for standard error difference. Test statistics of CSB were 4.696 for t-value, 8.013 for degree of freedom, 23.4578 ppm for mean difference and 4.9949 ppm for standard error difference. Test statistics of Tyvek® were 4.236 for t-value, 8.050 for degree of freedom, 18.0589 ppm for mean difference and 4.2630 ppm for standard error difference. Test statistics of cotton were 7.556 for t-value, 9 for degree of freedom, 165.0511 ppm for mean difference and 21.8443 ppm for standard error difference. Test statistics of denim in terms of penetration were –9.851 for t-value, 2.083 for degree of freedom, -82.0067 ppm for mean difference and 8.3257 ppm for standard error difference. The p-values showed the mean values of all six fabrics were significantly different when the weight was applied compared to no weight at 95 % confidence interval. The Mann-Whitney non-parametric test supported the same results (Table 4.21). All fabrics except SMS showed there was a significant difference at 95 % confidence interval whether weight was applied or not. Test statistics of the Wilcoxon test by using a grouping variable of weight to evaluate the difference in the mean with weight and the mean without weight found that all were statistically significant ($p < 0.05$). The Wilcoxon test gives a numeric value indicating how different the mean with weight and the mean without weight were. For cotton the Wilcoxon value was 3. MSB, CSB, and Tyvek® were 6 and denim was 45.

4.7.3 Atrazine and Chlorpyrifos (Percent Penetration) Using GC Data

Figure 10 and Figure 11 show the percent penetraton of atrazine and chlorpyrifos without and with weight using GC data. Data without weight was tranformed according to the equation suggested by John and Richard (1974). Levene's test for equal variances of atrazine and chlorpyrifos without weight percent penetration showed that all fabrics had equal variances except Tyvek®(Table 4. 22). A t-test was preferred to a non-parametric test to analyze the difference of mean percent penetration. The p-values showed the mean values of percent penetration of

Table 4.20 T-Test of Atrazine (ppm) between Without and With Weight Using HPLC Data

Levene's Test		T-test for Equality of Means						
		F	Sig.	t	df	Sig. (2 -tailed)	Mean Difference	Std. Error Difference
SMS	Equal variances assumed	9.729	.011	2.270	10	.047	19.3144	8.5082
	Equal variances not assumed			4.017	8.371	.004	19.3144	4.8084
MSB	Equal variances assumed	5.562	.040	2.288	10	.045	11.5000	5.0273
	Equal variances not assumed			4.074	8.157	.003	11.5000	2.8231
CSB	Equal variances assumed	9.926	.010	2.626	10	.025	23.4578	8.9320
	Equal variances not assumed			4.696	8.013	.002	23.4578	4.9949
Tyvek®	Equal variances assumed	9.484	.012	2.372	10	.039	8.0589	7.6149
	Equal variances not assumed			4.236	8.050	.003	18.0589	4.2630
Cotton	Equal variances assumed	.611	.454	7.556	9	.000	165.0511	21.8443
	Equal variances not assumed			13.349	5.330	.000	165.0511	12.3643
Denim	Equal variances assumed	7.938	.018	-17.256	10	.000	-82.0067	4.7525
	Equal variances not assumed			-9.851	2.083	.009	-82.0067	8.3250

Table 4.21 Mann-Whitney Test of Atrazine Penetration (ppm) between Without and With Weight Using HPLC Data

Fabric Type	Case	N	Mean Rank	Sum of Ranks
SMS	No. Weight	9	7.67	69.00
	Weight (2psi)	3	3.00	9.00
	Total	12		
MSB	No. Weight	9	8.00	72.00
	Weight (2psi)	3	2.00	6.00
	Total	12		
CSB	No. Weight	9	8.00	72.00
	Weight (2psi)	3	2.00	6.00
	Total	12		
Tyvek®	No. Weight	9	8.00	72.00
	Weight (2psi)	3	2.00	6.00
	Total	12		
Cotton	No. Weight	9	7.00	63.00
	Weight (2psi)	3	1.50	6.00
	Total	12		
Denim	No. Weight	9	5.00	45.00
	Weight (2psi)	3	11.00	33.00
	Total	12		

Test Statistics[c]			SMS	MSB	CSB	Tyvek®	Cotton	Denim
Mann-Whitney U			3.000	.000	.000	.000	.000	.000
Wilcoxon W			9.000	6.000	6.000	6.000	3.000	45.000
Z			-1.941	-2.505	-2.505	-2.496	-2.131	-2.496
Asymp. Sig. (2-tailed)			.052	.012	.012	.013	.033	.013
Exact Sig.[2*(1-tailed Sig.)]			.064[a]	.009[a]	.009[a]	.009[a]	.036[a]	.009[a]
Monte Carlo Sig. (2-tailed)	Sig.		.065[b]	.009[b]	.008[b]	.009[b]	.036[b]	.009[b]
	99% Confidence	Lower Bound	.058	.007	.006	.007	.031	.007
		Upper Bound	.071	.012	.011	.012	.040	.012
Monte Carlo Sig. (1-tailed)	Sig.		.033[b]	.005[b]	.004[b]	.005[b]	.018[b]	.005[b]
	99% Confidence	Lower Bound	.028	.003	.002	.003	.015	.003
		Upper Bound	.037	.007	.006	.007	.021	.006

a. Not corrected for ties

b. Based on 10000 sampled tables with starting seed 1441484369

c. Grouping Variable: CASE

d. Atrazine all fabrics were statistically significant by weight

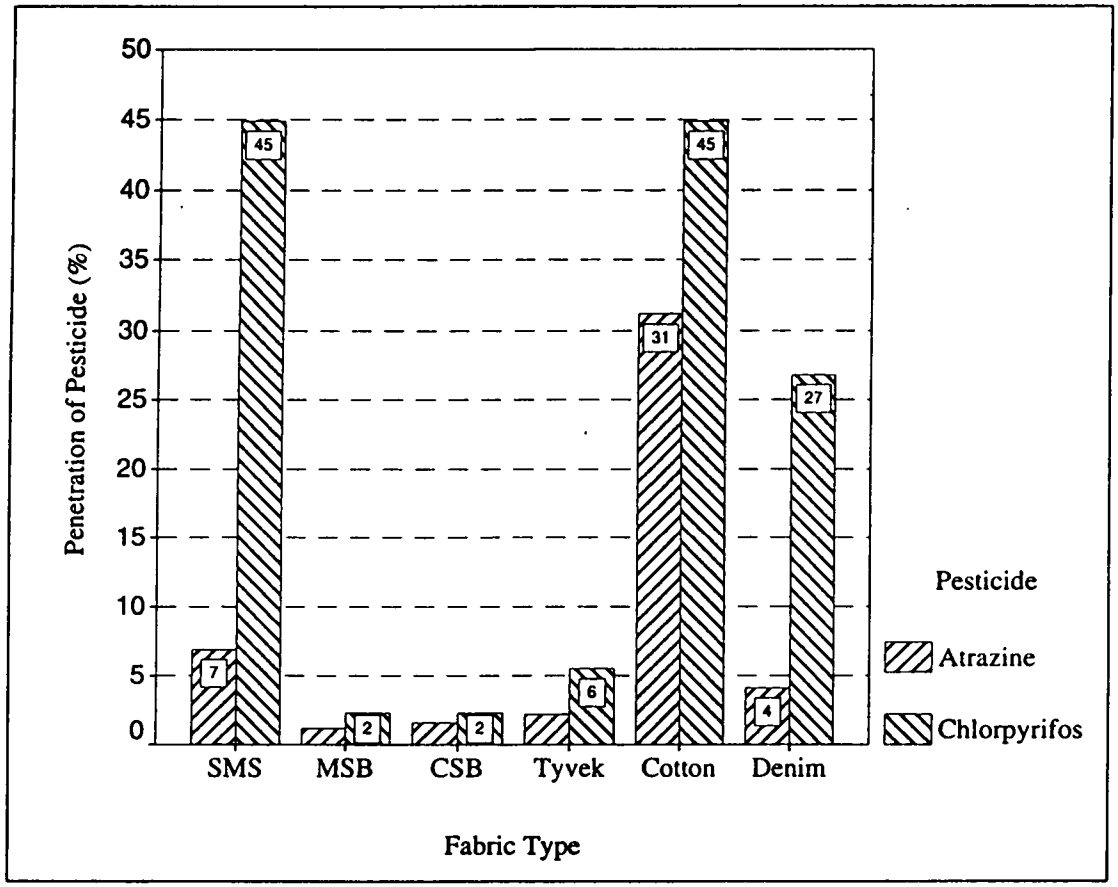


Figure 10 Atrazine and Chlorpyrifos Penetration (%) Without Weight Using GC Data

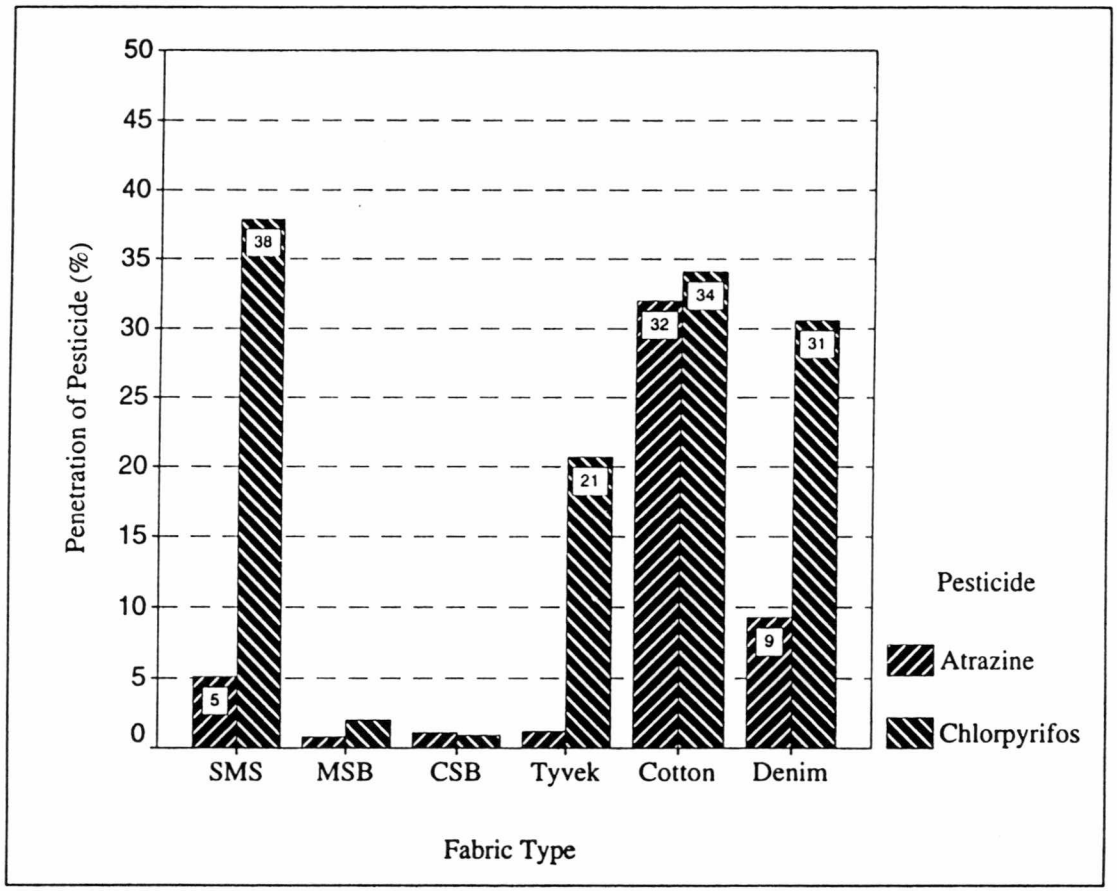


Figure 11 Atrazine and Chlorpyrifos Penetration (%) With Weight Using GC Data

Table 4.22 T-Test of Atrazine and Chlorpyrifos (%) Without Weight Using GC Data

Levene's Test		T-test for Equality of Means						
		F	Sig.	t	df	Sig. (2 -tailed)	Mean Difference	Std. Error Difference
SMS	Equal variances assumed	4.207	.070	-5.090	9	.001	-9.3683	.1840
	Equal variances not assumed			-5.600	5.298	.002	-9.3683	.1673
MSB	Equal variances assumed	.102	.756	-2.163	10	.056	-9.56E-02	4.420E-02
	Equal variances not assumed			-2.163	9.887	.056	-9.56E-02	4.420E-02
CSB	Equal variances assumed	.043	.839	-1.213	10	.253	-5.57E-02	4.597E-02
	Equal variances not assumed			-1.213	9.386	.255	-5.57E-02	4.597E-02
Tyvek®	Equal variances assumed	9.068	.013	-2.862	10	.017	-.0701	5.941E-02
	Equal variances not assumed			-2.862	7.185	.024	-.1701	5.941E-02
Cotton	Equal variances assumed	.767	.402	-5.854	10	.000	-.2803	4.789E-02
	Equal variances not assumed			-5.854	9.003	.000	-.2803	4.789E-02
Denim	Equal variances assumed	2.730	.129	-17.314	10	.000	-.6797	3.926E-02
	Equal variances not assumed			-17.314	7.325	.000	-.6797	3.926E-02

SMS, Tyvek®, cotton, and denim fabrics were significantly different in percent penetration whether atrazine or chlorpyrifos was applied at 95 % confidence interval. The p-value of SMS, Tyvek®, cotton, and denim showed the mean value of percent penetration was significantly different at the 95 % confidence interval (4.22). Test statistics of SMS were –5.090 for t-value, 9 for degree of freedom, -9.3683 % for mean difference and 0.1840 % for standard error difference. Test statistics of Tyvek® were –2.862 for t-value, 7.185 for degree of freedom, -0.1701 % for mean difference and 5.941E-02 % for standard error difference. Test statistics of cotton were –5.854 for t-value, 10 for degree of freedom, -0.2803 % for mean difference and 4.789E-02 % for standard error difference. Test statistics of denim were –17.314 for t-value, 10 for degree of freedom, -0.6797 % for mean difference and 3.926E-02 % for standard error difference. The Mann-Whitney non-parametric test supported the same results (Table 4.23). SMS, Tyvek®, cotton, and denim showed significant differences at 95% confidence interval. For SMS, Tyvek®, cotton and denim, test statistics of Wilcoxon test by using a grouping variable of pesticide type were 15.000, 24.000, 21.000 and 21.000. T-tests of atrazine and chlorpyrifos percent penetration with weight is shown in Table 4.24. Levene's test for equal variances of with weight percent penetration showed that SMS, Tyvek® and denim fabrics did not have equal variances and the other fabrics did. A t-test was preferred to a non-parametric test to analyze the difference of mean value. Test statistics of SMS were –4.827 for t-value, 5.087 for degree of freedom, -38.0395 % for mean difference and 7.8811 for standard error difference. Test statistics of Tyvek® were –2.750 for t-value, 6.155 for degree of freedom, -3.3949 % for mean difference and 1.2343 % for standard error difference. Test statistics of cotton were –5.847 for t-value, 10 for degree of freedom, -13.5353 % for mean difference and 2.3151 % for standard error difference. Test statistics of denim in terms of penetration were –14.408 for t-value, 10 for degree of freedom, -22.6407 % for mean difference and 1.5714 % for standard error difference. P-value for SMS, Tyvek®, cotton and denim showed the mean value of penetration was significantly different at 95% confidence interval. The mean values of the other fabrics were not. The Mann-Whitney non-parametric test showed that all fabrics were not significantly different at 95 % confidence interval (Table 4.25). It was probably due to the t-test being a strong and more confident test than the Mann-Whitney. In conclusion, atrazine and chlorpyrifos data analyzed using GC data without weight when analyzed using Mann-Whitney (Table 4. 23) showed that SMS, Tyvek®, cotton and denim were statistically different but MSB, CSB were not.

Table 4.23 Mann-Whitney Test of Atrazine and Chlorpyfiros Penetration (%) Without Weight Using GC Data

Fabric Type	Case	N	Mean Rank	Sum of Ranks
SMS	Atrazine	5	3.00	15.00
	Chlorpyrifos	6	8.50	51.00
	Total	11		
MSB	Atrazine	6	4.67	28.00
	Chlorpyrifos	6	8.33	50.00
	Total	12		
CSB	Atrazine	6	5.33	32.00
	Chlorpyrifos	6	7.67	46.00
	Total	12		
Tyvek®	Atrazine	6	4.00	24.00
	Chlorpyrifos	6	9.00	54.00
	Total	12		
Cotton	Atrazine	6	3.50	21.00
	Chlorpyrifos	6	9.50	57.00
	Total	12		
Denim	Atrazine	6	3.50	21.00
	Chlorpyrifos	6	9.50	57.00
	Total	12		

Test Statistics[c]			SMS	MSB	CSB	Tyvek®	Cotton	Denim
Mann-Whitney U			.000	7.000	11.000	3.000	.000	.000
Wilcoxon W			15.000	28.000	32.000	24.000	21.000	21.000
Z			-2.735	-1.761	-1.123	-2.406	-2.882	-2.882
Asymp. Sig. (2-tailed)			.006	.078	.261	.016	.004	.004
Exact Sig.[2*(1-tailed Sig.)]			.004[a]	.093[a]	.310[a]	.015[a]	.002[a]	.002[a]
Monte Carlo Sig. (2-tailed)	Sig.		.005[b]	.095[b]	.284[b]	.017[b]	.003[b]	.003[b]
	99% Confidence	Lower Bound	.003	.088	.272	.014	.002	.002
		Upper Bound	.007	.103	.295	.020	.004	.004
Monte Carlo Sig. (1-tailed)	Sig.		.002[b]	.048[b]	.149[b]	.009[b]	.002[b]	.002[b]
	99% Confidence	Lower Bound	.001	.043	.140	.007	.001	.001
		Upper Bound	.004	.054	.158	.012	.003	.003

a. Not corrected for ties

b. Based on 10000 sampled tables with starting seed 626550639

c. Grouping Variable: CASE

Table 4.24 T-Test of Atrazine and Chlorpyrifos (%) With Weight Using GC Data

Levene's Test		T-test for Equality of Means						
		F	Sig.	t	df	Sig. (2 -tailed)	Mean Difference	Std. Error Difference
SMS	Equal variances assumed	5.167	.049	-4.372	9	.002	-38.0395	8.7003
	Equal variances not assumed			-4.827	5.087	.005	-38.0395	7.8811
MSB	Equal variances assumed	.314	.588	-2.162	10	.056	-1.1626	.5378
	Equal variances not assumed			-2.162	9.394	.058	-1.1626	.5378
CSB	Equal variances assumed	.038	.849	-1.058	10	.315	-.6664	.6297
	Equal variances not assumed			-1.058	9.465	.316	-.6664	.6297
Tyvek®	Equal variances assumed	22.149	.001	-2.750	10	.020	-3.3949	1.2343
	Equal variances not assumed			-2.750	6.155	.032	-3.3949	1.2343
Cotton	Equal variances assumed	1.100	.319	-5.847	10	.000	-13.5353	2.3151
	Equal variances not assumed			-5.847	8.612	.000	-13.5353	2.3151
Denim	Equal variances assumed	7.648	.020	-14.408	10	.000	-22.6407	1.5714
	Equal variances not assumed			-14.408	5.507	.000	-22.6407	1.5714

Table 4.25 Mann-Whitney Test of Atrazine and Chlorpyfiros Penetration (%) With Weight Using GC Data

Fabric Type	Case	N	Mean Rank	Sum of Ranks
SMS	Atrazine	2	1.50	3.00
	Chlorpyrifos	1	3.00	3.00
	Total	3		
MSB	Atrazine	2	1.50	3.00
	Chlorpyrifos	2	3.50	7.00
	Total	4		
CSB	Atrazine	2	2.50	5.00
	Chlorpyrifos	2	2.50	5.00
	Total	4		
Tyvek®	Atrazine	2	1.50	3.00
	Chlorpyrifos	2	3.50	7.00
	Total	4		
Cotton	Atrazine	2	2.50	5.00
	Chlorpyrifos	2	2.50	5.00
	Total	4		
Denim	Atrazine	2	1.50	3.00
	Chlorpyrifos	2	3.50	7.00
	Total	4		

Test Statistics[c]			SMS	MSB	CSB	Tyvek®	Cotton	Denim
Mann-Whitney U			.000	.000	2.000	.000	2.000	.000
Wilcoxon W			3.000	3.000	5.000	3.000	5.000	3.000
Z			-1.225	-1.549	.000	-1.549	.000	-1.549
Asymp. Sig. (2-tailed)			.221	.121	1.000	.121	1.000	.121
Exact Sig.[2*(1-tailed Sig.)]			.667[a]	.333[a]	1.000[a]	.333[a]	1.000[a]	.333[a]
Monte Carlo Sig. (2-tailed)	Sig.		.666[b]	.326[b]	1.000[b]	.326[b]	1.000[b]	.326[b]
	99% Confidence	Lower Bound	.654	.314	1.000	.314	1.000	.314
		Upper Bound	.578	.338	1.000	.338	1.000	.338
Monte Carlo Sig. (1-tailed)	Sig.		.332[b]	.163[b]	.666[b]	.163[b]	.666[b]	.163[b]
	99% Confidence	Lower Bound	.320	.153	.654	.153	.654	.153
		Upper Bound	.344	.172	.678	.172	.678	.172

a. Not corrected for ties

b. Based on 10000 sampled tables with starting seed 651040138

c. Grouping Variable: CASE

4.7.4 Atrazine (GC and HPLC)

Figure 12 and Figure 13 show the atrazine penetrations without and with weight determined using a GC and a HPLC. When the percent penetration of atrazine using HPLC and GC were compared, the results were the same except for cotton. There were differences in percent penetration using a HPLC and GC when weight was applied. In the HPLC analysis, percent penetration of cotton was decreased about 12 percent when weight was applied. For other fabrics showed a little bit greater penetration than when using GC but the difference was not significant. Levene's test for equal variances showed penetration data of atrazine without weight when analyzed by GC and HPLC had equal variances except for denim indicating that a t-test was preferred to a non-parametric test to analyze the difference of mean value. Test statistics of cotton in terms of penetration were –3.157 for t-value, 13 for degree of freedom, -57.6744 ppm for mean difference and 18.2689 ppm for standard error difference (Table 4.26). P-value showed the mean value of cotton was significantly different at 95 % confidence interval for the GC data and the HPLC data. The mean values for the other fabrics were not. A Mann-Whitney non-parametric test supported the similar results (Table 4.27). Test statistic of the Wilcoxon test by using a grouping variable of analysis type of CSB were 29.000 and the p-value indicated that there was significant difference at 95 % confidence interval. Test statistic of the Wilcoxon test by using a grouping variable of analysis type of cotton were 25.000 and the p-value indicated that there was significant difference at 95 % confidence interval. The other fabrics were not significantly different whether a GC or HPLC was used. Levene's test for equal variances showed penetration data of atrazine between GC and HPLC with weight did not have equal variances except for denim, indicating that a non-parametric test was preferred to a t-test test to analyze the difference of mean rank. P-values showed the mean values of all fabrics were not significantly different at 95 % confidence interval whether a GC or HPLC was used (Table 4.28). A Mann-Whitney non-parametric test supported the same results (Table 4.29). P-value of all fabrics showed that there was no significant difference at 95 % confidence interval for a GC or HPLC.

4.7.5 Finish, Basis Weight and Thickness

A GLM test of pesticide penetration (ppm) was performed for finish type (Table 4.30). Test statistics were 127037.1 of squares, 1 for degree of freedom, 127037.1 for mean square, and p-value showed that there was significance different when finish was treated, especially for anti-static treatment. A GLM test of pesticide penetrations (ppm) was conducted for basis weight

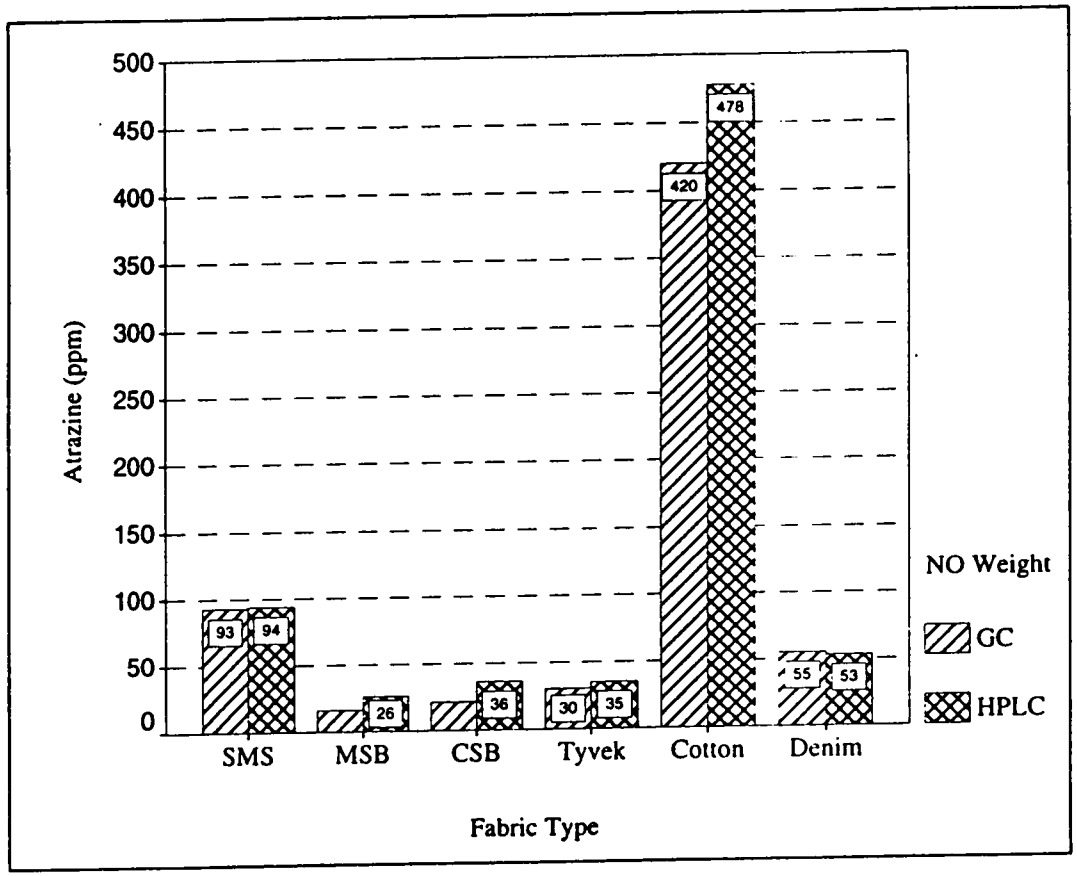


Figure 12 Atrazine Penetration Without Weight Determined Using GC and HPLC Data

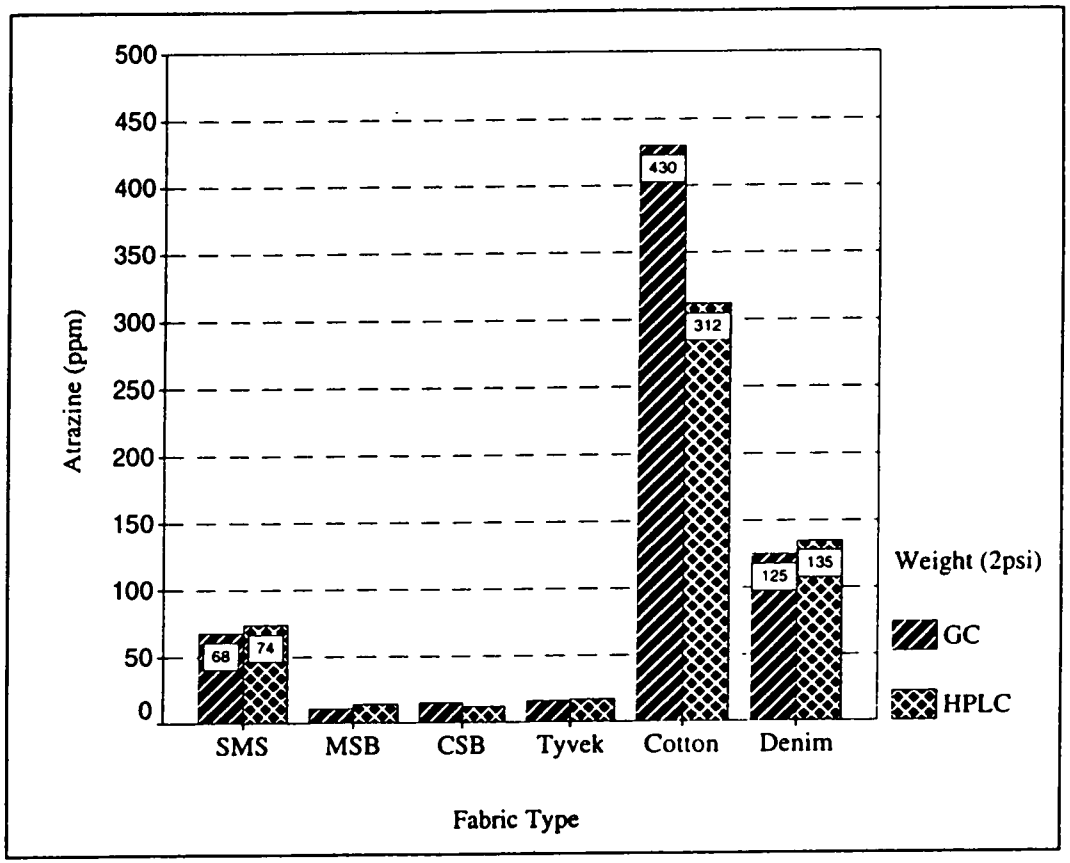


Figure 13 Atrazine Penetration With Weight Determined Using GC and HPLC Data

Table 4.26 T-Test of Atrazine (ppm) Without Weight Using GC and HPLC Data

Levene's Test		T-test for Equality of Means						
		F	Sig.	t	df	Sig. (2 -tailed)	Mean Difference	Std. Error Difference
SMS	Equal variances assumed	.956	.348	-.073	12	.943	-.6978	9.6146
	Equal variances not assumed			-.064	5.918	.951	-.6978	10.9352
MSB	Equal variances assumed	.269	.613	-2.044	13	.062	-10.1467	4.9647
	Equal variances not assumed			-1.938	8.947	.085	-10.1467	5.2349
CSB	Equal variances assumed	.185	.674	-1.809	13	.094	-14.7878	8.1738
	Equal variances not assumed			-1.776	10.185	.106	-14.7878	8.3261
Tyvek®	Equal variances assumed	.192	.668	-.747	13	.469	-5.0856	6.8113
	Equal variances not assumed			-.742	10.625	.474	-5.0856	6.8565
Cotton	Equal variances assumed	1.394	.259	-3.157	13	.008	-57.6744	18.2689
	Equal variances not assumed			-2.935	8.289	.018	-57.6744	19.6525
Denim	Equal variances assumed	4.747	.048	.480	13	.639	1.9200	4.0004
	Equal variances not assumed			.400	5.654	.704	1.9200	4.7964

Table 4.27 Mann-Whitney Test of Atrazine (ppm) Without Weight Using GC and HPLC Data

Fabric Type	Case	N	Mean Rank	Sum of Ranks
SMS	GC	5	7.20	36.00
	HPLC	9	7.67	69.00
	Total	14		
MSB	GC	6	5.50	33.00
	HPLC	9	9.67	87.00
	Total	15		
CSB	GC	6	4.83	29.00
	HPLC	9	10.11	91.00
	Total	15		
Tyvek®	GC	6	7.33	44.00
	HPLC	9	8.44	76.00
	Total	15		
Cotton	GC	6	4.17	25.00
	HPLC	9	10.56	95.00
	Total	15		
Denim	GC	6	8.17	49.00
	HPLC	9	7.89	71.00
	Total	15		

Test Statistics[c]			SMS	MSB	CSB	Tyvek®	Cotton	Denim
Mann-Whitney U			21.000	12.000	8.000	23.000	4.000	26.000
Wilcoxon W			36.000	33.000	29.000	44.000	25.000	71.000
Z			-.200	-1.769	-2.241	-.471	-2.715	-.118
Asymp. Sig. (2-tailed)			.841	.077	.025	.637	.007	.906
Exact Sig.[2*(1-tailed Sig.)]			.898[a]	.088[a]	.026[a]	.689[a]	.005[a]	.955[a]
Monte Carlo Sig. (2-tailed)	Sig.		.899[b]	.081[b]	.024[b]	.691[b]	.005[b]	.957[b]
	99% Confidence	Lower Bound	.891	.074	.020	.679	.003	.952
		Upper Bound	.906	.088	.028	.703	.006	.962
Monte Carlo Sig. (1-tailed)	Sig.		.448[b]	.040[b]	.011[b]	.347[b]	.002[b]	.479[b]
	99% Confidence	Lower Bound	.431	.035	.008	.335	.001	.466
		Upper Bound	.461	.045	.013	.359	.003	.492

a. Not corrected for ties

b. Based on 10000 sampled tables with starting seed 1238861123

c. Grouping Variable: CASE

Table 4.28 T-Test of Atrazine (ppm) With Weight Using GC and HPLC Data

Levene's Test		T-test for Equality of Means						
		F	Sig.	t	df	Sig. (2 -tailed)	Mean Difference	Std. Error Difference
SMS	Equal variances assumed	381.947	.000	-.931	3	.421	-6.5833	7.0708
	Equal variances not assumed			-.698	1.012	.611	-6.5833	9.4289
MSB	Equal variances assumed	457.293	.000	-1.629	3	.202	-3.6300	2.2283
	Equal variances not assumed			-1.225	1.018	.433	-3.6300	2.9633
CSB	Equal variances assumed	20203.350	.000	.325	3	.767	2.1200	6.5244
	Equal variances not assumed			.242	1.001	.849	2.1200	8.7511
Tyvek®	Equal variances assumed	1616.263	.000	-.159	3	.884	-.8767	5.5243
	Equal variances not assumed			-.118	1.002	.925	-.8767	7.4039
Cotton	Equal variances assumed	1.35E+16	.000	2.114	2	.169	117.4600	55.5640
	Equal variances not assumed			2.114	1.038	.274	117.4600	55.5640
Denim	Equal variances assumed	.313	.615	-.827	3	.469	-9.7200	11.7523
	Equal variances not assumed			-.915	2.945	.429	-9.7200	10.6206

Table 4.29 Mann-Whitney Test of Atrazine (ppm) With Weight Using GC and HPLC Data

Fabric Type	Case	N	Mean Rank	Sum of Ranks
SMS	GC	2	3.00	6.00
	HPLC	3	3.00	9.00
	Total	5		
MSB	GC	2	1.50	3.00
	HPLC	3	4.00	12.00
	Total	5		
CSB	GC	2	3.00	6.00
	HPLC	3	3.00	9.00
	Total	5		
Tyvek®	GC	2	3.00	6.00
	HPLC	3	3.00	9.00
	Total	5		
Cotton	GC	2	3.50	7.00
	HPLC	3	1.50	3.00
	Total	5		
Denim	GC	2	2.00	4.00
	HPLC	3	3.67	11.00
	Total	5		

Test Statistics[c]			SMS	MSB	CSB	Tyvek®	Cotton	Denim
Mann-Whitney U			3.000	.000	3.000	3.000	.000	1.000
Wilcoxon W			9.000	3.000	9.000	9.000	3.000	4.000
Z			.000	-1.777	.000	.000	-1.549	-1.155
Asymp. Sig. (2-tailed)			1.000	.076	1.000	1.000	.121	.248
Exact Sig.[2*(1-tailed Sig.)]			1.000[a]	.200[a]	1.000[a]	1.000[a]	.333[a]	.400[a]
Monte Carlo Sig. (2-tailed)	Sig.		1.000[b]	.199[b]	1.000[b]	1.000[b]	.341[b]	.404[b]
	99% Confidence	Lower Bound	1.000	.189	1.000	1.000	.329	.391
		Upper Bound	1.000	.209	1.000	1.000	.353	.417
Monte Carlo Sig. (1-tailed)	Sig.		.608[b]	.103[b]	.599[b]	.608[b]	.171[b]	.204[b]
	99% Confidence	Lower Bound	.595	.095	.586	.595	.161	.194
		Upper Bound	.620	.111	.612	.620	.181	.214

a. Not corrected for ties

b. Based on 10000 sampled tables with starting seed 533845165

c. Grouping Variable: CASE

Table 4.30 General Linear Model of Pesticide Penetration (ppm) Separated by Finish

Source	Sum of Squares	df	Mean Square	F	Sig.
Conc.(ppm) Main Effects Finish	127037.1	1	127037.1	7.567	.007
Model	127037.1	1	127037.1	7.567	.007
Residual	2736673	163	14767.985		
Total	2863711	164	17461.650		

a. Conc. by Finish

b. All effects entered simultaneously

(Table 4.31). Test statistics were 2118603 for sum of squares, 4 for degree of freedom, 529650.8 for mean square and p-value showed that there was a significant difference by basis weight. A correlation test conducted at 99 % confidence interval among pesticide penetration, fabric type, finish, basis weight and thickness (Table 4.32) showed that pesticide penetration was affected by fabric type and finish treatment.

SUMMARY OF RESULTS

The purpose of this study was to determine if different fabrics provide various degrees of protection against pesticide penetration whether a 2 psi weight was applied or not. The order of the barrier resistance of the fabrics against atrazine was (MSB and CSB), Tyvek®1422, SMS, denim, and cotton knit. There were no differences whether weight was applied or not except with denim. The barrier efficiency of denim decreased about twice when 2 psi pressure was applied for one minute. The fabric order of the barrier resistance to chlorpyrifos was (MSB and CSB), Tyvek®1422, denim, SMS, and cotton knit. There were no differences whether weight was applied except with Tyvek®1422 and cotton knit. The barrier efficiency of Tyvek®1422 decreased about three times and the barrier efficiency of cotton knit increased slightly when a 2 psi pressure was applied for one minute. Similar results were obtained using GC and HPLC. To compare the percent penetration of both atrazine and chlorpyrifos, the order of the barrier efficiency of the fabrics without weight applied was (MSB and CSB), denim, Tyvek®1422, SMS, and cotton knit. The order of the barrier efficiency of the fabrics was (MSB and CSB), Tyvek®1422, denim, cotton knit, and SMS when weight was applied. The barrier efficiencies of all fabrics were decreased against chlorpyrifos compared to atrazine. Cotton and denim showed similar barrier efficiency against chlorpyrifos when the 2 psi weight was applied for one minute. The barrier efficiency of SMS decreased dramatically when a 2 psi weight was applied for one minute. MSB, CSB and Tyvek®1422 showed good barrier efficiencies against atrazine and chlorpyrifos. Denim had good protection against atrazine while it was not enough against chlorpyrifos. Cotton had the worst protection ranged about 30 to 40 percent penetration of atrazine and chlorpyrifos no matter whether weight was applied or not. Protection of denim against atrazine was decreased almost twofold when weight was applied even for one minute. SMS nonwoven showed the worst protection among those nonwovens. It had a good protection against atrazine but the penetration of chlorpyrifos was 35 to 45 percent, which was even larger than denim. In general agricultural

Table 4.31 General Linear Model of Pesticide Penetration (ppm) Separated by Basis Weight

Source	Sum of Squares	df	Mean Square	F	Sig.	Observed Power[a]
Corrected Model	2118603[b]	4	529650.8	113.734	.000	1.000
Intercept	1770221	1	1770221	380.127	.000	1.000
Basis Weight	2118603	4	529650.8	113.734	.000	1.000
Error	745107.4	160	4656.921			
Total	4465986	165				
Corrected Total	2863711	164				

a. Computed using alpha = .05

b. R Squared = .740 (Adjusted R Squared = .733)

c. Dependent Variable: Conc. (ppm)

Table 4.32 Correlation Among Pesticide Penetration (ppm), Fabric Type, Finish, Basis Weight and Thickness

Pearson Correlation	Conc.	Sig. (2-tailed)	N
Conc.	1.000	.	165
Fabric	.327**	.000	165
Finish	-.211**	.000	165
Basis Weight	.106	.177	165
Thickness	.095	.224	165

**. Correlation is significant at the 0.01 level (2-tailed)

applications, SMS nonwoven, denim and cotton were not good protective clothing while they had a good barrier protection against certain pesticide. MSB, CSB and Tyvek®1422 had good protection. MSB and CSB had a excellent barrier efficiency against both atrazine and chlorpyrifos while Tyvek®1422 had a excellent efficiency against only atrazine. Finish treatment affected the pesticide penetration but basis weight and thickness did not.

DISCUSSION

Percent penetration of chlorpyrifos was larger than that of atrazine in most cases. It was assumed that the different chemical characteristics of the two pesticides behaved differently in penetration through the fabrics. Chlorpyrifos, (6.62 % (v/v), active ingredient) was dissolved in xylene and polyglycol and then it was diluted to 1.0 % with distilled water. Atrazine (40.8 % (v/v), active ingredient) was dissolved in water. Chlropyrifos 1.0 % (v/v) solution was more hydrophobic than was atrazine 2.5 % (v/v) solution. In the case of polypropylene SMS, which is hydrophobic, chlorpyrifos solution penetration was high as expected. Barrier efficiency of SMS was decreased more than six times against chlorpyrifos than atrazine. It was probably affected by the hydrophobic characteristic of the polypropylene SMS. Most spunbond and meltblown layers are made of one hundred percent polypropylene except for tiny amounts of other lubricating materials, which helps in processing. Swelling effect of polypropylene may contribute to the high level of chlorpyrifos retention by decreasing fiber crystallinity and allowing the chlorpyrifos to enter the inter-chain regions (Dell, 1993). Cotton knit had the worst barrier efficiency against both atrazine and chlorpyrifos. Atrazine has most potential hydrogen bonding site in its structure and cotton has hydrophlic hydroxyl groups (-OH) but cotton knit and denim acted differently against atrazine. Denim showed good barrier efficiency against atrazine but knit was not. The sturcture of the fabric seemed to affect strongly penetration of atrazine in case of cotton. Knit fabric had more open structure than denim twill that knit allowed the atrazine solution more easily. In the case of denim, a similar assumption was applied to that of cotton knit. Pesticide penetration against atrazine was larger than most nonwovens because it is hydrophilic. However, the penetration rate of denim against chlorpyrifos was more than twice as large as that of atrazine. The penetration rate of cotton knit and denim was increased against chlorpyrifos when a 2 psi weight was applied for one minute. Especially the penetration of denim increased dramatically. It was assumed that chemical or physical characteristics of the inert components in the pesticide

solution would affect penetration. The pressure applied onto fabric seemed to accelerate the swelling effect. According to Kim's research (1997), the mechanism of binding between atrazine and fabric seemed not to governed by hydrogen bonding but to governed London force like van der waal's attraction between molecules of atrazine and fabric that good barrier efficiency of denim against atrazine agreed this.

CHAPTER V

CONCLUSION AND RECOMMENDATIONS

5.1 CONCLUSION

This study was limited to only two pesticides. Each pesticide was tested at a different concentration. Concentration used in this study was the concentration that was recommended by the manufacturer. Each active ingredient of the pesticide used in this study was limited to only one type of formulation. In addition, the weight application did not show any significant differences except cotton and denim. It might be beneficial to repeat this study with a larger sample size. It is recommended that inert materials in the pesticides should be analyzed in depth. The formulations of the pesticides are reported in the MSDS of each pesticide, but the inert ingredients are not. It seemed that the characteristics of the inert components affect the chemical or other properties of pesticide solution when it is mixed with water, which influences largely the penetration of pesticide. Surfactants can especially influence the liquid properties if a very small amount is added. Therefore it seemed important to investigate the characteristics of the surfactants not only itself but also in the mixture with the other active ingredients, inert ingredients and water.

5.2 RECOMMENDATIONS FOR FUTURE STUDIES

1. Further studies could be done with larger sample sizes.
2. The weight test could be done in different time applications such as from one to ten minutes, which might differentiate the penetration efficiency of the nonwovens.
3. It is recommended that one choose the pesticides with the same active ingredient from different types of formulations: granular, emulsifiable concentrate, flowable liquid ingredients, which might aid to investigate the effects of the other inert components.
4. It is recommended that one choose the pesticides with the same active ingredient from different concentrations of active ingredients, which might be helpful to analyze the effect of the other ingredients.

5. It will be useful to use real human or animal skin samples as a second layer to analyze how much pesticides are penetrating through the skin, if real human or animal skin samples are available.

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APPENDICES

APPENDIX A

MSDS of Atrazine 4L®

RESTRICTED USE PESTICIDE
(GROUND AND SURFACE WATER CONCERNS)

FOR RETAIL SALE TO AND USE ONLY BY CERTIFIED APPLICATORS OR PERSONS UNDER THEIR DIRECT SUPERVISION AND ONLY FOR THOSE USES COVERED BY THE CERTIFIED APPLICATOR'S CERTIFICATION.

THIS PRODUCT IS A RESTRICTED USE HERBICIDE DUE TO GROUND AND SURFACE WATER CONCERNS. USERS MUST READ AND FOLLOW ALL PRECAUTIONARY STATEMENTS AND INSTRUCTIONS FOR USE IN ORDER TO MINIMIZE POTENTIAL FOR ATRAZINE TO REACH GROUND AND SURFACE WATER.

ATRAZINE 4L HERBICIDE

For Season-Long Weed Control In Corn, Sorghum, and Certain Other Crops.

KEEP OUT OF REACH OF CHILDREN
CAUTION

REFER TO INSIDE OF LABEL BOOKLET FOR ADDITIONAL PRECAUTIONARY STATEMENTS AND DIRECTIONS FOR USE, INCLUDING STORAGE AND DISPOSAL.

ACTIVE INGREDIENTS:	
Atrazine: 2-chloro-4-ethylamino-6-isopropylamino-s-triazine	40.8%
Related Compounds	2.2%
INERT INGREDIENTS	57.0%
Total	100.0%

Atrazine 4L Contains 4 Lbs. Active Ingredients Per Gallon.
Shake Well Before Using. Use Entire Contents At One Time.

Net Contents: 2 1/2 Gallons

EPA Reg. No. 1386-647

EPA Est. No. Used Corresponds To Letter in Lot No.: A-1386-OH-1 B-9779-AR-13

CO-OP

Universal Cooperatives, Inc. Minneapolis, MN 55440

PRECAUTIONARY STATEMENTS
HAZARDS TO HUMANS AND DOMESTIC ANIMALS
CAUTION

Harmful if swallowed, inhaled or absorbed through skin. Do not breathe vapors or spray mist. Avoid contact with eyes, skin or clothing.

Personal Protective Equipment (PPE)

Applicators and other handlers (other than mixers and loaders) must wear:

- Long-sleeved shirt and long pants
- Water-proof gloves
- Chemical-resistant footwear plus socks

Mixers and loaders must wear:

- Long-sleeved shirt and long pants
- Water-proof gloves
- Chemical-resistant footwear plus socks
- Protective eyewear

Follow manufacturer's instructions for cleaning/maintaining PPE. If no such instructions for washables, use detergent and hot water. Keep and wash PPE separately from other laundry.

Engineering Control Statements

When handlers use closed systems, enclosed cabs, or aircraft in a manner that meets the requirements listed in the Worker Protection Standard (WPS) for agricultural pesticides [40 CFR 170.240 (d) (4-6)], the handler PPE requirements may be reduced or modified as specified in the WPS.

USER SAFETY RECOMMENDATIONS

Users should:

- Wash hands before eating, drinking, chewing gum, using tobacco or using the toilet.
- Remove clothing immediately if pesticide gets inside. Then wash thoroughly and put on clean clothing.
- Remove PPE immediately after handling this product. Wash the outside of gloves before removing. As soon as possible wash thoroughly and change into clean clothing.

STATEMENT OF PRACTICAL TREATMENT

If swallowed: Call a physician or Poison Control Center immediately. Drink 1 or 2 glasses of water and induce vomiting by touching back of throat with finger, or, if available, by administering syrup of ipecac. Do not induce vomiting or give anything by mouth to an unconscious person.

If inhaled: Remove victim to fresh air. If not breathing, give artificial respiration, preferably mouth-to-mouth. Get medical attention.

If on skin: Wash with plenty of soap and water. Get medical attention.

If in eyes: Flush eyes with plenty of water. Call a physician if irritation persists.

Note to Physician: There is no specific antidote for atrazine. If this product is ingested, induce emesis or lavage stomach. The use of an aqueous slurry of activated charcoal may be considered.

For Medical Emergency only, call 1-800-228-5635, extension 138.

ENVIRONMENTAL HAZARDS

Atrazine can travel (seep or leach) through soil and can enter ground water which may be used as drinking water. Atrazine has been found in ground water. Users are advised not to apply atrazine to sand and loamy sand soils where the water table (ground water) is close to the surface and where these soils are very permeable, i.e., well-drained. Your local agricultural agencies can provide further information on the type of soil in your area and the location of ground water.

This product may not be mixed/loaded or used within 50 ft. of all wells, including abandoned wells, drainage wells, and sink holes.

This product may not be mixed or loaded within 50 ft. of intermittent streams and rivers, natural or impounded lakes and reservoirs. This product may not be applied aerially or by ground within 66 ft. of the points where field surface water runoff enters perennial or intermittent streams and rivers or within 200 ft. around natural or impounded lakes and reservoirs. If this product is applied to highly erodible land, the 66-ft. buffer or setback from runoff entry points must be planted to crop, seeded with grass, or other suitable crop.

This pesticide is toxic to aquatic invertebrates. Do not apply directly to water, to areas where surface water is present, or to intertidal areas below the mean high water mark. Do not apply when weather conditions favor drift from treated areas. Runoff and drift from treated areas may be hazardous to aquatic organisms in neighboring areas. Do not contaminate water when disposing of equipment wash waters.

DIRECTIONS FOR USE

It is a violation of Federal law to use this product in a manner inconsistent with its labeling.

Do not apply this product in a way that will contact workers or other persons, either directly or through drift. Only protected handlers may be in the area during application. For any requirements specific to your State or Tribe, consult the agency responsible for pesticide regulation.

AGRICULTURAL USE REQUIREMENTS

Use this product only in accordance with its labeling and with the Worker Protection Standard, 40 CFR part 170. This Standard contains requirements for the protection of agricultural workers on farms, forests, nurseries, and greenhouses, and handlers of agricultural pesticides. It contains requirements for training, decontamination, notification, and emergency assistance. It also contains specific instructions and exceptions pertaining to the statements on this label about personal protective equipment (PPE) and restricted-entry interval. The requirements in this box only apply to uses of this product that are covered by the Worker Protection Standard.

Do not enter or allow worker entry into treated areas during the restricted-entry interval (REI) of 12 hours.

PPE required for early entry to treated areas that is permitted under the Worker Protection Standard and that involves contact with anything that has been treated, such as plants, soil, or water is:

- Coveralls
- Water-proof gloves
- Chemical resistant footwear plus socks

NON-AGRICULTURAL USE REQUIREMENTS

The requirements in this box apply to uses of this product that are NOT within the scope of the Worker Protection Standard for agricultural pesticides (40 CFR Part 170). The WPS applies when this product is used to produce agricultural plants on farms, forests, nurseries, or greenhouses.

Do not enter treated areas without protective clothing until sprays have dried.

FAILURE TO FOLLOW THE DIRECTIONS FOR USE AND PRECAUTIONS ON THIS LABEL MAY RESULT IN POOR WEED CONTROL, CROP INJURY, OR ILLEGAL RESIDUES.

DO NOT APPLY THIS PRODUCT THROUGH ANY TYPE OF IRRIGATION SYSTEM.

General Information

This herbicide controls many annual broadleaf and grass weeds in corn, sorghum, sugarcane, and certain other crops specified on this label. This product may be applied before or after weeds emerge.

Following many years of continuous use of this product and chemically related products, biotypes of some of the weeds listed on this label have been reported which cannot be effectively controlled by this and related herbicides. Where this is known or suspected, and weeds controlled by this product are expected to be present along with resistant biotypes, we recommend the use of this product in combinations or in sequence with other registered herbicides which are not triazines. If only resistant biotypes are expected to be present, use a registered non-triazine herbicide. Consult with your state Agricultural Extension Service for specific recommendations.

Since this product acts mainly through root absorption, its effectiveness depends on moisture to move it into the root zone. If weeds develop, a shallow cultivation or rotary hoeing will generally result in better weed control.

This product is noncorrosive to equipment and metal surfaces, nonflammable, and has low electrical conductivity.

Avoid using near adjacent desirable plants or in greenhouses, or injury may occur.

To avoid spray drift, do not apply under windy conditions. Avoid spray overlap, as crop injury may result.

Where the use directions give a range of rates, use the lower rate on coarse-textured soil and soil low in organic matter; use the higher rate on fine-textured soil and soil high in organic matter.

NOTE: Universal Cooperatives, Inc., does not recommend applications in combination with other herbicides or oils, except as specifically described on the label.

Application Procedures

Ground application: Use conventional ground sprayers equipped with nozzles that provide accurate and uniform application. Be certain that nozzles are uniformly spaced and are the same size. Calibrate sprayer before use and recalibrate at the start of each season and when changing carriers. Unless otherwise specified, use a minimum of 10 gals. of spray mixture per acre for all preplant incorporated, preplant surface, preemergence, and postemergence applications (with or without oil or surfactant) with ground equipment.

Use a pump with capacity to: (1) maintain 35-40 psi at nozzles, (2) provide sufficient agitation in tank to keep mixture in suspension, and (3) to provide a minimum of 20% bypass at all times. Use centrifugal pumps which provide propeller shear action for dispersing and mixing this product. The pump should provide a minimum of 10 gals./minute/100 gal. tank size circulated through a correctly positioned sparger tube or jets.

Use screens to protect the pump and to prevent nozzles from clogging. Screens placed on the suction side of the pump should be *16-mesh or coarser*. Do not place a screen in the recirculation line. Use 50-mesh or coarser screens between the pump and boom, and where required, at the nozzles. Check nozzle manufacturer's recommendations.

For band applications, calculate amount to be applied per acre as follows:

$$\frac{\text{band width in inches}}{\text{row width in inches}} \times \text{broadcast rate per acre} = \text{amount needed per acre of field}$$

Aerial application: Use aerial application only where broadcast applications are specified. Apply in a minimum of 1 qt. of water for each qt. of this product applied per acre. For postemergence treatments on corn and sorghum, apply recommended rate in a minimum of 2 gals. of water per acre. Avoid applications under conditions where uniform coverage cannot be obtained or where excessive spray drift may occur.

Avoid application to humans or animals. Flagmen and loaders should avoid inhalation of spray mist and prolonged contact with skin.

Application in water or liquid fertilizer: Nitrogen solution or complete liquid fertilizer may replace all or part of the water as a carrier for preemergence, preplant incorporated, or preplant surface ground application on corn and sorghum. Check the compatibility of this product with liquid fertilizer and/or nitrogen solution as shown below before use. Do not apply in nitrogen solution or complete liquid fertilizer after corn or sorghum emerges, or crop injury may occur.

Compatibility Test: Since liquid fertilizers can vary even within the same analysis, always **check compatibility with herbicide(s) each time before use.** Be especially careful when using complete suspension or fluid fertilizers as serious compatibility problems are more likely to occur. Commercial application equipment may improve compatibility in some instances. The following test assumes a spray volume of 25 gals./A. For other spray volumes, make appropriate changes in the ingredients. Check compatibility using this procedure.

1. Add 1 pt. of fertilizer to each of 2 one qt. jars with tight lids.
2. To one of the jars add 1/4 teaspoon or 1.2 milliliters of a compatibility agent approved for this use, such as Kem Link (1/4 teaspoon is equivalent to 2 pints per 100 gallons spray). Shake or stir gently to mix.
3. To both jars add the appropriate amount of herbicide(s). If more than one herbicide is used, add them separately with dry herbicides first, flowables next, and emulsifiable concentrates last. After each addition, shake or stir gently to thoroughly mix. The appropriate amount of herbicides for this test follows:

   Dry herbicides: For each pound to be applied per acre, add 1.5 level teaspoons to each jar.
   Liquid herbicides: For each pint to be applied per acre, add 0.5 teaspoon or 2.5 milliliters to each jar.
4. After adding all ingredients, put lids on and tighten, and invert each jar 10 times to mix. Let the mixtures stand 15 minutes and then look for separation, large flakes, precipitates, gels, heavy oily film on the jar, or other signs of incompatibility. Determine if the compatibility agent is needed in the spray mixture by comparing the 2 jars. If either mixture separates, but can be remixed readily, the mixture can be sprayed as long as good agitation is used. If the mixtures are incompatible, test the following methods of improving compatibility: (A) slurry the dry herbicide(s) in water before addition, or (B) add 1/2 of the compatibility agent to the fertilizer and the other 1/2 to the emulsifiable concentrate or flowable herbicide before addition to the mixture. If incompatibility is still observed, do not use the mixture.

Application in water plus emulsifiable oil or oil concentrate: Adding emulsifiable oil (petroleum-derived, petroleum-derived oil concentrate, or single or mixed crop-derived oil concentrate) to postemergence water-based sprays in corn and sorghum may improve weed control. However, under certain conditions, the use of either type of oil may seriously injure the crop. To minimize this possibility, observe the following directions:

Use one of the following properly emulsified:

1. A suitable oil concentrate containing at least 1% but not more than 20% suitable emulsifier or surfactant blend.
2. Petroleum-derived oil containing at least 1% suitable emulsifier.

NOTE: In the event of a compatibility problem when mixing oil with this product and water, a compatibility agent such as Kem Link should be used. Any of the above oils contaminated with water or other materials can cause compatibility problems and/or crop injury.

Mixing procedures – all uses: (1) Be sure sprayer is clean and not contaminated with any other materials, or crop injury or sprayer clogging may result. (2) Fill tank 1/4 full with clean water, nitrogen solution, or complete liquid fertilizer. (3) Start agitation. (4) Be certain that the agitation system is working properly and creates a rippling or rolling action on the liquid surface. (5) Pour product directly from container into tank. (6) Continue filling tank until 90% full. Increase agitation if necessary to maintain surface action. (7) Add emulsifiable oil, oil concentrate, or tank mix herbicide(s) after this product is thoroughly suspended. (8) Finish filling tank. (9) Empty tank as completely as possible before refilling to prevent buildup of oil or emulsifiable concentrate residue. Maintain agitation to avoid separation of materials. (10) If an oil or emulsifiable concentrate film starts to build up in tank, drain it and clean with strong detergent solution or solvent. (11) Clean sprayer thoroughly immediately after use by flushing system with water containing a detergent.

Rotational Crops – All Uses: (1) Do not rotate to any crop except corn or sorghum until the following year, or injury may occur. (2) If applied after June 10, do not rotate with crops other than corn or sorghum the next year, or crop injury may occur. (3) In the High Plains and Intermountain areas of the West where rainfall is sparse and erratic or where irrigation is required, use only when corn or sorghum is to follow corn or sorghum or when a crop of untreated corn or sorghum is to precede other rotational crops. (4) In eastern parts of the Dakotas, KS, western MN, and NE, do not rotate to soybeans if the rate applied to corn or sorghum was more than 2.2 pounds/A or equivalent band application rate, or soybean injury may occur. (5) Injury may occur to soybeans planted the year following application on soils having a calcareous surface layer. (6) Do not plant sugar beets, tobacco, vegetables (including dry beans), spring-seeded small grains, or small-seeded legumes and grasses the year following application, or injury may occur.

Atrazine 4L Applied Alone – Corn or Grain Sorghum*

Preplant Surface-Applied, Preplant Incorporated, or Preemergence (or Postemergence at 4 pts./A With Oil)

Broadleaf and Grass Weeds Controlled

barnyardgrass (watergrass)***
giant foxtail**
green foxtail***
large (hairy) crabgrass**
wild oats
witchgrass (*Panicum capillare*)***
yellow foxtail***
cocklebur**
groundcherry
jimsonweed
kochia
lambsquarters
annual morningglory
mustards
nightshade
pigweed
purslane
ragweed
sicklepod**
velvetleaf
(buttonweed)***

Postemergence with Emulsifiable Oil or Oil Concentrate in Water (at 2.4 pts./A)

Broadleaf Weeds Controlled

annual morningglory
cocklebur
jimsonweed
lambsquarters
mustards
pigweed
ragweed
smartweed
wild buckwheat
velvetleaf**

* Where there are state/local requirements regarding atrazine use (including lower maximum rates and/or greater setbacks) which are different from the label, the more restrictive/protective requirements must be followed. Certain states may have established rate limitations within specific geographical areas. Consult your state lead pesticide control agency for additional information. It is a violation of this label to deviate from state use regulations.

** Partial control only.

*** Partial control only on medium- and fine-textured soils.

Corn

Preplant Surface-Applied (Broadleaf and grass control): Use on medium- and fine-textured soil with minimum-tillage or no-tillage systems only in CO, IA, IL, IN, KS, KY, MN, MO, MT, ND, NE, SD, WI, and WY. Apply the recommended rate of Atrazine 4L shown in Table 1 up to 45 days prior to planting. On *coarse-textured soils*, do not apply more than 2 weeks prior to planting. If an unsatisfactory length of weed control results from adverse environmental conditions following early treatment, a follow-up application of an appropriately labeled herbicide may be used. If the follow-up treatment includes atrazine, do not exceed the labeled rate for corn indicated in Table 1.

If weeds are present at the time of treatment, apply in tank mix combination with a contact herbicide (for example, Gramoxone® Extra or Roundup®). Observe directions for use, precautions, and restrictions on the label of the contact herbicide.

Note: To the extent possible, do not move treated soil out of the row or move untreated soil to the surface during planting, or weed control will be diminished.

Preplant Incorporated (Broadleaf and grass control): Broadcast in spring after plowing at rate in Table 1. Apply to the soil and incorporate before, during, or after final seedbed preparation. Avoid deep incorporation. For best results, apply within 2 weeks prior to planting.

Preemergence or At-Planting (Broadleaf and grass control): Apply during or shortly after planting before weed emergence, at rate in Table 1.

Postemergence (Broadleaf and grass control): Apply before weeds exceed 1.5 inches in height and before corn exceeds 12 inches in height at rate in Table 1.

Table 1: Broadleaf and Grass Weed Control in Corn*

FOR ALL SOIL APPLICATIONS PRIOR TO CROP EMERGENCE

- **On Highly Erodible Soils (as defined by SCS)**

  If conservation tillage is practiced, leaving at least 30% of the soil covered with plant residues at planting, apply a maximum of 4 pts./A as a broadcast spray.

  If the soil coverage with plant residue is less than 30% at planting, a maximum of 3.2 pts./A may be applied.

- **On Soils Not Highly Erodible**

  Apply 4 pts./A as a broadcast spray.

FOR POSTEMERGENCE APPLICATION

If no atrazine was applied prior to corn emergence, apply a maximum of 4 pts./A broadcast. If a postemergence treatment is required following an earlier herbicide application, the total atrazine applied may not exceed 2.5 lbs. active ingredient (5 pts. of this product) per acre per calendar year.

* *Broadleaf control: eastern CO, western KS, western NE, NM, OK panhandle, west TX, and eastern WY:* On sand, loamy sand, sandy loam, mild to strongly alkaline soil, and all recently leveled soil, apply no more than 2.4 pts./A, either preplant surface, preplant incorporated, or preemergence. On other soils in these areas, apply rate in Table 1 for broadleaf and grass control.

Where there are state/local requirements regarding atrazine use (including lower maximum rates and/or greater setbacks) which are different from the label, the more restrictive/protective requirements must be followed. Certain states may have established rate limitations within specific geographical areas. Consult your state lead pesticide control agency for additional information. It is a violation of this label to deviate from state use regulations.

Postemergence with emulsifiable oil or oil concentrate in water: Add the following volume of one of the type oils indicated for aerial or ground application unless the oil label specifies otherwise.

Type Oil	Ground Application	Aerial Application
Oil Concentrate (Crop or Petroleum-derived)	1 qt./A	1/2 - 1 qt./A
Petroleum-derived oil	1 gal./A	2 qts./A

Note: Crop-derived or petroleum-derived oil concentrates should contain at least 1%, but not more than 20%, suitable emulsifier or surfactant blend. Petroleum-derived oils should contain at least 1% suitable emulsifier.

Broadleaf and grass control: For postemergence control of those weeds listed under **Preplant Incorporated and Preemergence**, broadcast 4 pts./A plus emulsifiable oil or oil concentrate after weed emergence but before weeds reach 1.5 inches in height and before corn exceeds 12 inches in height.

Broadleaf control: For postemergence control of those weeds listed under **Postemergence with emulsifiable oil or oil concentrate in water**, broadcast 2.4 pts./A plus emulsifiable oil or oil concentrate before pigweed and lambsquarters reach 6 inches in height and before all other weeds reach 4 inches in height. A cultivation may be necessary if all weeds are not controlled or if weeds regrow.

Precautions: For applications with emulsifiable oil or oil concentrate in water: (1) Inbred lines or any breeding stock may be severely injured by applications with emulsifiable oil or oil concentrate. (2) Adding other insecticides, herbicides, liquid fertilizers, or other materials is not recommended, because they may cause compatibility problems or crop injury. (3) Store and handle emulsifiable oil and oil concentrate carefully. Oil contaminated with even a small amount of water may not emulsify properly when added to the tank. To avoid crop injury, (4) Do not apply when crop is under stress from prolonged cold, wet weather, poor fertility, or other factors, or when crop is wet and succulent from recent rainfall. (5) Do not exceed 2.5 lbs. active ingredient (or 5 pts. of this product) per acre per calendar year. (6) Postemergence applications to corn must be made before corn exceeds 12 inches in height.

Tank Mixtures for Corn

This product may be tank mixed with these herbicides for control of certain broadleaf and grass weeds in corn

Dual® (metolachlor)	Lasso or Lasso EC + Roundup
Dual + Gramoxone Extra	Lasso or Lasso EC + Gramoxone Extra
Dual + Roundup (glyphosate)	Gramoxone Extra
Dual + Princep®	Princep
Dual + Princep + Gramoxone Extra	Princep + Gramoxone Extra
Dual + Princep + Roundup	Princep + Roundup
Bexton® or Ramrod® (propachlor)	Roundup
Lasso® or Lasso EC (alachlor)	Sutan +®

Use tank mix directions appearing on the labels of the above herbicides when tank mixing with this product. Observe all precautions and limitations on labeling of products used in a particular tank mix.

NOTE: When the labels of the above herbicides refer to Atrazine 80W, use equivalent rates of Atrazine 4L. One pound of 80W equals 1.6 pints of 4L.

Princep 80W, Princep 4L, or Princep Caliber 90®

In addition to the weeds listed under **Atrazine 4L Applied Alone - Corn or Grain Sorghum - Preplant Surface-Applied, Preplant Incorporated, or Preemergence**, this combination also controls crabgrass, fall panicum, and carpetweed.

Broadcast tank mix before planting, at planting, or after planting, but before crop and weeds emerge, at rates in Table 2. Use the 1:1 ratio for control of most weeds. Use the 1:2 ratio for expected heavy infestations of crabgrass and fall panicum. Cultivate shallowly if weeds develop.

Preplant Surface-Applied: Use on medium- and fine-textured soils with minimum-tillage or no-tillage systems only in CO, IA, IL, IN, KS, KY, MN, MO, MT, ND, NE, SD, WI, and WY. Apply the recommended rate of Atrazine 4L and Princep shown in Table 2 up to 45 days prior to planting. Refer to the Atrazine 4L alone section for information if weeds should develop following the early treatment. On *coarse-textured soils*, do not apply more than 2 weeks prior to planting. Refer to the **Atrazine 4L Applied Alone - Preplant Surface-Applied** section of the corn label for additional details.

If weeds are present at time of treatment, apply in a tank mix combination with a contact herbicide (for example, Gramoxone Extra or Roundup). Observe directions for use, precautions, and restrictions on the label of the contact herbicide.

Note: To the extent possible, do not move treated soil out of the row or move untreated soil to the surface during planting, or weed control will be diminished.

Preplant Incorporated: Apply to the soil and incorporate in the spring before, during, or after final seedbed preparation. Avoid deep incorporation. For best results, apply within 2 weeks prior to planting.

Preemergence: Apply during or shortly after planting, but before crop and weeds emerge.

Refer to Corn sections of this label and to Princep 80W, Princep Caliber 90, or Princep 4L labels for further directions, limitations, and precautions.

Table 2: Tank Mixtures with Princep on Corn

Soil Texture	Broadcast Rate/A			
	1:1 Ratio*		1:2 Ratio**	
	This Product	Princep 80W†	This Product	Princep 80W†
Sand, loamy sand, sandy loam	2 pts	1.25 lbs	1.32 pts	1.67 lbs
Loam, silt loam, silt, clay loam, sandy clay loam, silty clay loam, sandy clay, or silty clay with low organic matter	2.4 pts	1.5 lbs.	1.6 pts	2 lbs.
Loam, silt loam, silt, clay loam, sandy clay loam, silty clay loam, sandy clay, or silty clay with medium to high organic matter, and clay (including dark prairie soils of the Corn Belt)	3 pts	1.8 lbs	1.92 pts	2.4 lbs.

* For control of most weeds

** For control of expected heavy infestations of crabgrass and fall panicum

† When using Princep Caliber 90 or Princep 4L, use equivalent rates. One lb. of Princep 80W equals 0.9 lb. of Princep Caliber 90 or 1.6 pts. of Princep 4L.

Princep 80W, Princep 4L, or Princep Caliber 90 plus Roundup: Use as tank mixture for preemergence and postemergence control of certain broadleaf and grass weeds where corn will be planted directly into a cover crop, established sod, or in previous crop residues. Refer to Roundup label for all directions, weeds controlled, precautions, and limitations.

Princep 80W, Princep 4L, or Princep Caliber 90 plus Gramoxone Extra: Use as tank mixture with Princep and Gramoxone Extra to kill existing vegetation and for residual weed control where corn will be planted directly into a cover crop, established sod, or in previous crop residues. Add this product and Princep to water in spray tank, agitating until thoroughly mixed. Then, add Gramoxone Extra and a nonionic surfactant, such as Aquagene 90. Continue agitation during application. Broadcast 2-4 pts. of this product plus 1.25-2.5 lbs. of Princep 80W (or 2-4 pts. of Princep 4L, or 1 1-2 2 lbs. of Princep Caliber 90) plus a suitable amount of Gramoxone Extra in 20-60 gals. of water per sprayed acre. Refer to the Gramoxone Extra label for the appropriate rates to utilize in this tank mixture. Apply before, during, or after planting, but before corn emerges. Add 0.5 pt. of a nonionic surfactant, such as Aquagene 90, per 100 gals. of spray mixture. Use the higher rate of Gramoxone Extra specified on the label if existing vegetation is 4-6 inches tall. This mixture will not control weeds taller than 6 inches.

Refer to further limitations and precautions on labels for this product, Princep, and Gramoxone Extra

Precautions: For all applications to corn: (1) To avoid crop injury and illegal residues, do not apply more than 2.5 lbs./A active ingredient (5 pts./A of this product) per calendar year. (2) For best control of velvetleaf and cocklebur, the application rate cannot be less than 2 lbs./A active ingredient, either alone or in tank mix combinations. (3) Following harvest, plow (moldboard or disk-plow) and thoroughly till soil in fall or spring to minimize possible injury to spring-seeded rotational crops, regardless of rate used.

Note for all applications to corn: Do not graze or feed forage from treated areas for 21 days following application, or illegal residues may result.

Sorghum and Sorghum-sudan Hybrids (Grain and Forage Types)

Preplant Surface-Applied (Broadleaf and grass control): Use on medium- and fine-textured soil with minimum-tillage or no-tillage systems only in CO, IA, IL, IN, KS, KY, MN, MO, MT, ND, NE, SD, WI, and WY. Apply the recommended rate of Atrazine 4L shown in Table 3 up to 45 days prior to planting. If an unsatisfactory length of weed control results from adverse environmental conditions following early treatment, a follow-up application of an appropriately labeled herbicide may be used. If the follow-up treatment includes atrazine, do not exceed the labeled rate for corn indicated in Table 1. Under dry conditions, irrigation after application is recommended to move Atrazine 4L into the soil.

If weeds are present at time of treatment, apply in a tank mix combination with a contact herbicide (for example, Gramoxone Extra or Roundup). Observe directions for use, precautions, and restrictions on the label of the contact herbicide.

Note: To the extent possible, do not move treated soil out of the row or move untreated soil to the surface during planting, or weed control will be diminished.

Preplant Incorporated (Broadleaf and grass control): Broadcast in spring after plowing at rate shown in Table 3. Apply before, during, or after final seedbed preparation. If soil is tilled or worked after application, avoid deep incorporation. For best results, apply within 2 weeks prior to planting.

Preemergence or At-Planting (Broadleaf and grass control): Apply during or shortly after planting, but prior to weed or crop emergence at rate shown in Table 3.

Postemergence (Broadleaf and grass control): Apply at rate shown in Table 3 before weeds exceed 1.5 inches in height and before sorghum exceeds 12 inches in height.

Table 3: Broadleaf and Grass Weed Control in Sorghum[1,2]

FOR ALL SOIL APPLICATIONS PRIOR TO CROP EMERGENCE

- **On Highly Erodible Soils (as defined by SCS)**

  If conservation tillage is practiced, leaving at least 30% of the soil covered with plant residues at planting, apply a maximum of 4 pts./A as a broadcast spray.

  If the soil coverage with plant residue is less than 30% at planting, a maximum of 3.2 pts./A may be applied.

- **On Soils Not Highly Erodible**

  Apply 4 pts./A as a broadcast spray.

FOR POSTEMERGENCE APPLICATION

If no atrazine was applied prior to sorghum emergence, apply a maximum of 4 pts./A broadcast. If a postemergence treatment is required following an earlier herbicide application, the total atrazine applied may not exceed 2.5 lbs. active ingredient (5 pts. of this product) per acre per calendar year.

[1]Do not apply preplant surface or preplant incorporated in AL, AR, FL, GA, LA, MS, NC, NM, OK, SC, TN, or TX. Do not apply preemergence in NM, OK, or TX, except in northeast OK and the TX Gulf Coast and Blacklands areas.

[2]Where there are state/local requirements regarding atrazine use (including lower maximum rates and/or greater setbacks) which are different from the label, the more restrictive/protective requirements must be followed. Certain states may have established rate limitations within specific geographical areas. Consult your state lead pesticide control agency for additional information. It is a violation of this label to deviate from state use regulations.

In case of planting failure, sorghum or corn may be replanted. Do not make a second broadcast application, or injury may occur. If originally applied in a band and sorghum or corn is replanted in untreated row middles, this product may be applied in a band to the second planting provided the maximum application rate of 2.5 lbs. ai/A atrazine per calendar year is not exceeded.

Preemergence broadleaf weed control in furrow irrigated bedded sorghum (AZ and CA only): For preemergence control of many broadleaf weeds, broadcast 1.6-2.4 pts./A after bed preparation, during or after planting, but before sorghum and weeds emerge and before the first furrow irrigation. Follow with several regular irrigations, making sure to thoroughly wet all soil.

Precautions for preemergence application to furrow irrigated bedded sorghum in AZ and CA. To avoid possible sorghum injury, do not use on sand or loamy sand soil or on sorghum planted in furrows. Applications to sorghum growing on alkali soils or where cuts, fills, or erosion have exposed calcareous or alkali subsoils may cause crop injury. In case of crop failure, do not replant sorghum for 8 months following application. Corn may be planted immediately.

Postemergence broadleaf weed control with emulsifiable oil or oil concentrate in water: Broadcast 2.4 pts./A for control of many broadleaf weeds. Apply before pigweed and lambsquarters reach 6 inches in height and before all other weeds reach 4 inches in height. In CO, western KS, NM, OK, TX, and desert regions of AZ and CA, apply when sorghum is 6-12 inches in height. In all other areas, apply after sorghum reaches the 3-leaf stage, but before it exceeds 12 inches in height. Add 1 gal. of emulsifiable oil per acre for ground application and 0.5 gal./A for aerial application, or add 1 qt./A of oil concentrate for ground application. A cultivation may be necessary if all weeds are not controlled or if weeds regrow.

For the list of weeds controlled, see **Atrazine 4L Applied Alone - Corn or Grain Sorghum - Postemergence with Emulsifiable Oil or Oil Concentrate in Water.**

Precautions for applications with emulsifiable oil or oil concentrate in water See "Precautions for applications with emulsifiable oil or oil concentrate in water" in Corn section

Postemergence broadleaf weed control with surfactant (CO, western KS, NM, OK, TX, and desert regions of AZ and CA only): Broadcast 2 4 pts /A plus 0 75-1 5 pts of surfactant after sorghum reaches 6 inches in height, but before weeds exceed 1 5 inches in height. Apply only on sandy loam and finer textured soil

Precautions For all applications to sorghum (1) Heavy rain immediately following application tends to cause excessive concentrations of herbicide in seed furrow resulting in possible crop injury Do not apply to furrow planted sorghum until furrows are leveled (plowed in) Level deep planter marks or seed furrows before application (2) Application to sorghum growing under stress caused by minor element deficiency or to sorghum growing on highly calcareous soil may result in crop injury (3) Following harvest, plow (moldboard or disk-plow) and thoroughly till soil in fall or spring to minimize possible injury to spring-seeded rotational crops, regardless of rate used (4) Injury may occur if both this herbicide, preplant surface, preplant incorporated, or preemergence, and an at-planting systemic insecticide applied in-furrow are used (5) Do not apply more than 2 5 lbs active ingredient (5 pts of this product) per acre per calendar year (6) For all soil applications prior to crop emergence (except for preemergence use on bedded sorghum in AZ and CA), do not apply to coarse textured soils, i e , sand, loamy sand, sandy loam, or to medium- and fine-textured soils having less than 1% organic matter, or injury may occur (7) For postemergence applications, do not apply to sand or loamy sand, or injury may occur.

Note: Do not graze or feed forage from treated areas for 21 days following application, or illegal residues may result.

Tank Mixtures for Grain Sorghum

Dual 8E: Use as tank mixture with Dual 8E for control of those weeds listed on the Dual 8E label, as well as on this label. Use this tank mixture only on sorghum seed treated with Concep® Refer to the Dual 8E label for all directions, precautions, and limitations.

Winter Weed Control in Texas

For postemergence control of winter weeds only, such as henbit, seedling dock, and annual thistle on fall bedded land in the Gulf Coast and Blacklands of TX Apply 0 8-1 qt /A postemergence to the weeds in November or December to land that will be planted to corn, grain sorghum, or forage sorghum the following spring For best results, add a suitable surfactant, such as Aquagene 90, at the rate of 0 5% of the spray volume, an emulsifiable oil at the rate of 1 0% of the spray volume, or an oil concentrate at the rate of 1 qt /A.

Normal weed control programs may be used in the following corn, grain sorghum, or forage sorghum crop.

Note: Do not plant any crops except corn, grain sorghum, or forage sorghum the spring following this treatment, or illegal residues may result

Atrazine 4L Alone - Chemical Fallow

Wheat-Sorghum-Fallow: To control annual broadleaf and grass weeds following wheat harvest and in the following sorghum crop when grown under minimum tillage broadcast 6 pts /A to wheat stubble immediately following wheat harvest If weeds are present at application, remove them with a sweep plow or other suitable implement after application, or use an approved contact herbicide before or after the application of Atrazine 4L. Plant sorghum into wheat stubble the following spring with minimum soil disturbance Use a surface planter or a planter leaving a shallow furrow If weeds are present at planting, remove them with a sweep plow or other suitable implement before planting.

For the list of weeds controlled, see **Atrazine 4L Applied Alone - Corn or Grain Sorghum - Preplant Surface-Applied, Preplant Incorporated, or Preemergence.**

Precautions (1) Use only on silt loam or finer textured soil or crop injury may result (2) Wheat-sorghum-fallow cropping sequence must be followed (3) Do not apply following sorghum harvest

Note: To avoid illegal residues, do not graze or feed forage from treated area to livestock. To avoid illegal residues and crop injury, do not plant any crop other than those on this label within 18 months following treatment.

Wheat-Corn-Fallow (KS, NE): This product controls cheatgrass (downy brome, chess), kochia, mustards, pigweed, Russian thistle, wild lettuce, wild sunflower, and volunteer wheat during period after wheat harvest Weed control may extend into following corn crop grown under minimum tillage

Follow directions for use, notes, and precautions in the **Wheat-Sorghum-Fallow** section above, substituting corn for references to sorghum.

Wheat-Fallow-Wheat (CO, KS, ND, NE, SD, and WY): For preemergence control of cheatgrass (downy brome, chess), common lambsquarters, field pennycress, kochia, mustard, Russian thistle, wild lettuce, and suppression of volunteer wheat during fallow period of a wheat-fallow-wheat rotation, broadcast 1-2 pts /A on all soils except those listed under *Precautions* For control of pigweed and wild sunflower, use the higher rate. Apply to stubble ground Treat only once during same fallow period

Tank Mixtures for Chemical Fallow

Wheat-Sorghum-Fallow or Wheat-Corn-Fallow (KS, NE)

Gramoxone Extra: If weeds are present at application, a tank mix with Gramoxone Extra may be used Broadcast 6 pts of Atrazine 4L plus a suitable amount of Gramoxone Extra in 20-60 gals of water per acre by ground equipment. Add 0 5-1 pt of a nonionic surfactant, such as Aquagene 90, per 100 gals of spray mixture Add Atrazine 4L to spray tank first and thoroughly mix with water Then add Gramoxone Extra, followed by surfactant. Use the higher rate of Gramoxone Extra specified on the label if weeds are 4-6 inches tall This mixture will not control weeds taller than 6 inches Apply to stubble ground Treat only once during same fallow period Refer to Gramoxone Extra label for further directions, precautions, and limitations

Wheat-Fallow-Wheat (CO, KS, ND, NE, SD, and WY)

Gramoxone Extra: If weeds are present at application, a tank mix with Gramoxone Extra may be used Broadcast 1-2 pts. of Atrazine 4L plus a suitable amount of Gramoxone Extra in 20-60 gals of water per acre by ground equipment. Add 0 5-1 pt of a nonionic surfactant, such as Aquagene 90, per 100 gals of spray mixture Add Atrazine 4L to spray tank first and thoroughly mix with water. Then add Gramoxone Extra, followed by surfactant Use the higher rate of Gramoxone Extra specified on the label if weeds are 4-6 inches tall. This mixture will not control weeds taller than 6 inches Apply to stubble ground Treat only once during same fallow period Refer to Gramoxone Extra label for further directions, precautions, and limitations.

If weeds are present at application and this product is used alone, use either an approved contact herbicide before or after treatment, or tillage after treatment

Use tillage to control weeds which escape during fallow period Till before planting For this product applied alone or in tank mixture with Gramoxone Extra plant at least 2 inches deep and 12 months or more after application

Precautions To avoid crop injury, (1) Do not use on sand soil (2) Do not treat eroded hillsides, caliche and rocky outcroppings, or exposed calcareous subsoil (3) Do not treat soils of the Rosebud and Canyon Series in western NE and adjoining counties in CO and WY. (4) Do not treat soils with calcareous surface layers (5) Avoid spray overlap

Note: Do not graze treated areas within 6 months after application, or illegal residues may result

Aerial application: In order to assure that spray will be controllable within the target area when used according to label directions, make applications at a maximum height of 10 ft., using low drift nozzles at a maximum pressure of 40 psi, and restrict application to periods when wind speed does not exceed 10 mph To assure that spray will not adversely affect adjacent sensitive nontarget plants, apply Atrazine 4L alone by aircraft at a minimum upwind distance of 400 ft. from sensitive plants

Roadsides

To control certain annual weeds in established perennial grasses along roadsides in CO, KS, MT, ND, NE, SD, and WY, including cheatgrass (downy brome, chess), common (annual) broomweed, little barley, medusahead, sagewort, and tumble mustard, broadcast 2 pts /A in a minimum of 10 gals of water by ground equipment in the fall before ground freezes or after thawing in the spring, but before the established grasses green-up and before weeds emerge Examples of desirable established grasses include big bluestem, bluegrama, bromegrass, buffalograss, crested wheatgrass, indiangrass, little bluestem, side-oats grama, switchgrass, and western wheatgrass Apply only once per year Temporary discoloration or other form of injury to the desirable perennial grasses may occur following application

Notes: To avoid illegal residues, (1) Do not cut or feed roadside grass hay (2) Do not allow livestock to graze treated areas

Sugarcane

For control of many broadleaf and grass weeds, including amaranths, crabgrass, fireweed, Flora's paintbrush, foxtails, junglerice, and wiregrass, broadcast 4-8 pts /A of Atrazine 4L at time of planting or ratooning, but before sugarcane emerges Broadcast aerially in a minimum of 5 gals of spray per acre, or broadcast or band by ground equipment in a minimum of 20 gals /A, unless indicated otherwise One additional application may be made over the sugarcane as it emerges, and 2 additional applications may be made interline after emergence as directed sprays Repeat treatments, where needed, may be applied broadcast, band, or interline as suggested with the final application being prior to close-in Do not exceed the rate of herbicide suggested for any one crop of sugarcane

Note: Where high rates of Atrazine 4L are used alone, apply in a minimum of 1 qt of water for each 1 qt. of Atrazine 4L applied per acre

Aerial application: In order to assure that spray will be controllable within the target area when used according to label directions, make applications at a maximum height of 10 ft., using low drift nozzles at a maximum pressure of 40 psi, and restrict application to periods when wind speed does not exceed 10 mph To assure that spray will not adversely affect adjacent sensitive nontarget plants, apply Atrazine 4L alone by aircraft at a minimum upwind distance of 400 ft. from sensitive plants

Florida

For control of emerged pellitory weed Apply 0 8-1 2 pts /A in at least 40 gals of water as a directed spray by ground equipment prior to close-in. Add 4 qts of surfactant for each 100 gals of spray Thoroughly cover weed foliage

For control of alexandergrass, large crabgrass, pellitory (artillery) weed, and spiny amaranth, use one of the following methods at planting or ratooning:

1 Apply 8 pts /A preemergence Follow with 1 or 2 applications, as needed, postemergence to sugarcane and weeds, at 4 pts /A. Treat before weeds exceed 1 5 inches in height

2 Apply 1-3 times, as needed, at 4 pts /A postemergence to sugarcane and weeds Treat before weeds exceed 1 5 inches in height.

Louisiana

For control of annual weeds during the summer fallow period, apply 4 pts /A to weed-free beds immediately after bed formation. Follow normal weed control program after planting

Precautions To avoid crop injury, (1) Do not apply more than 10 qts /A to any one crop of sugarcane (2) If making 4 pts /A application during summer fallow period, do not exceed 8 qts /A during the remainder of the growing season, or illegal residues may result.

Texas

Use Atrazine 4L for control of barnyardgrass, pigweed, purslane, and sunflower, in plant or ratoon sugarcane.

Apply 8 pts /A of Atrazine 4L preemergence Follow with 1 or 2 applications, as needed, at 6 pts /A post-emergence to sugarcane and weeds.

For best results when weeds are emerged, add a nonionic surfactant at a concentration of 2 qts /100 gals. to the spray and apply before weeds exceed 1 5 inches in height

Precautions (1) Injury to sugarcane may occur when under moisture stress, when soil is of low absorptive capacity, or when land is first cropped to sugarcane (2) Do not apply after close-in (3) Do not apply more than 20 pts /A to any one crop of sugarcane, or crop injury may result.

Turfgrasses for Sod (Florida only)

St. Augustinegrass, Centipedegrass, and Zoysiagrass

Broadcast 4-8 pts /A according to soil texture to control those weeds listed under **Atrazine 4L Applied Alone - Corn or Grain Sorghum - Preplant Surface-Applied, Preplant Incorporated, or Preemergence**

Muck or peat	8 pts	Old beds Within 2 days after lifting sod
		New beds 3-4 days after sprigging or plugging
Sandy soil	4 pts	Old beds Within 2 days after lifting sod
		New beds 7-10 days after sprigging or plugging

If weeds regrow, apply an additional 4 pts /A on muck or peat, or 2 pts /A on sandy soil.

Precautions To avoid crop injury, (1) Do not apply within 30 days prior to cutting or lifting (2) Do not apply in combination with surfactants or other spray additives (3) Use only on turfgrass reasonably free of infestations of insects, nematodes, and diseases (4) On newly sprigged turfgrass, temporary slowing of growth may follow application

Turfgrass for Fairways, Lawns, Sod Production*, and Similar Areas

*In states other than FL For use on turfgrass for sod in FL, see Turfgrasses for Sod (Florida only) section.

Bermudagrass, Centipedegrass, St. Augustinegrass, and Zoysiagrass

Apply Atrazine 4L after October 1 before emergence of winter annual weeds for control of annual bluegrass, burclover, carpet burweed, chickweed corn speedwell, henbit, hop clover, and spurweed Atrazine 4L will control annual bluegrass even if it is emerged at time of treatment For control of summer annual weeds listed in the preemergence section of the **Atrazine 4L Applied Alone - Corn or Grain Sorghum** section of this label, also apply Atrazine 4L in late winter before the weeds emerge Apply in a minimum of 15 gals. of water per acre or 1 gal. per 1,000 sq. ft.

Where annual bluegrass is the major weed, use 1 qt /A (22 ml or 0.75 fl. oz per 1,000 sq. ft.) Use 2 qts /A (44 ml or 1.5 fl. oz per 1,000 sq. ft.) for control of the other weeds named above Do not exceed 1 qt /A per treatment on newly sprigged turfgrass or on hybrid bermudagrass such as Tiflawn, Tifway, and Ormond

For continued summer annual weed control, apply another 1 qt /A at least 30 days after the previous application, but not after April 15. However, do not make more than 2 applications of this product per year

Precautions On newly sprigged turfgrass and hybrid bermudagrass, temporary slowing of growth and yellowing may occur following application. To avoid turf injury, (1) Use only on turfgrass reasonably free of infestations of insects, nematodes, and diseases (2) Do not use on golf greens (3) Do not use north of NC (except may be used in VA Coastal Plains) or west of the high rainfall areas of eastern OK and eastern TX. (4) Do not use on muck or alkaline soils (5) Do not apply over the rooting area of trees or ornamentals not listed on this label. (6) Do not overseed with desirable turfgrass within 4 months before or 6 months after treatment (7) Do not apply this product to newly seeded bermudagrass until it has overwintered and has a well-developed rhizome system. Do not exceed 2 qts product per acre within 12 months of seeding bermudagrass.

Note: Do not graze or feed turf clippings to animals, or illegal residues may result

Macadamia Nuts

For preemergence control of many broadleaf and grass weeds, including crabgrass, foxtail, wiregrass, Flora's paintbrush, spanishneedles, and fireweed, broadcast 4-8 pts /A before harvest and before weeds emerge Repeat as necessary Do not spray when nuts are on ground during harvest period. Do not apply by air.

Guava

Use only on established plantings which are at least 18 months old Apply as a directed spray at 4-8 pts /A of Atrazine 4L in 20-50 gals. of spray mix preemergence or early postemergence to weeds When applying postemergence, the use of a surfactant and greater spray volume (80-100 gals. of spray mix per acre) may enhance weed control This product controls many annual broadleaf and grass weeds, including fireweed, purslane, scarlet pimpernel, spanishneedles, and sowthistle

Notes: To avoid illegal residues (1) Do not allow spray to contact foliage or fruit. (2) Do not apply more frequently than at 4 month intervals (3) Do not apply more than 16 pts. of Atrazine 4L per year

Conifers

For control of annual broadleaf and grass weeds prior to transplanting, after transplanting, or in established conifers (including Douglas fir, grand fir, noble fir, white fir, Austrian pine, bishop pine, Jeffrey pine, knobcone pine, loblolly pine, lodgepole pine (shore pine), monterey pine, ponderosa pine, Scotch pine, slash pine, blue spruce, and Sitka spruce) Broadcast 4-8 pts in a minimum of 5 gals. of water per acre by air or 10 gals. by ground before weeds are 1.5 inches tall Apply to established trees between fall and early spring while trees are dormant For new transplants, apply during or soon after transplanting For applications prior to transplanting, allow sufficient precipitation to activate Atrazine 4L before transplanting. In areas where spring and summer rainfall is inadequate to activate Atrazine 4L, apply during fall prior to spring transplanting.

For the list of weeds controlled, see **Atrazine 4L Applied Alone - Corn or Grain Sorghum - Preplant Surface-Applied, Preplant Incorporated, or Preemergence**

Quackgrass control: Broadcast 8 pts in a minimum of 5 gals. of water per acre by air or 10 gals. by ground between fall and early spring while trees are dormant and before quackgrass is more than 1.5 inches tall

Precautions (1) In areas west of the Rocky Mountains (except the Great Basin), grazing may begin 7 months after a fall application or 3 months after a winter or spring application (2) To prevent illegal residues, do not graze treated areas of the Great Basin, or areas east of the Rocky Mountains. (3) Temporary injury to trees may occur following use of Atrazine 4L on coarse-textured soil (4) To avoid crop injury, do not apply to seedbeds (5) Also apply only once per year.

Aerial application: In order to assure that spray will be controllable within the target area when used according to label directions, make applications at a maximum height of 10 ft above vegetation, using low drift nozzles at a maximum pressure of 40 psi, and restrict application to periods when wind speed does not exceed 10 mph. To assure that spray will not adversely affect adjacent sensitive nontarget plants, apply Atrazine 4L by aircraft at a minimum upwind distance of 400 ft. from sensitive plants.

STORAGE AND DISPOSAL

Storage

Ground water contamination may be reduced by diking and flooring of permanent liquid bulk storage sites with an impermeable material.

Pesticide Disposal

Do not contaminate water, food, or feed by storage or disposal, or cleaning of equipment. Open dumping is prohibited. Wastes resulting from the use of this product are acutely toxic. Improper disposal of unused pesticide, spray mixture, or rinsate is a violation of Federal law. Pesticide, spray mixture, or rinsate that cannot be used according to label instructions must be disposed of according to Federal, State, or local procedures. For guidance in proper disposal methods, contact your State Pesticide or Environmental Control Agency, or the Hazardous Waste representative at the nearest EPA Regional Office.

Container Disposal

Triple rinse (or equivalent) and offer for recycling or reconditioning, or puncture and dispose of in a sanitary landfill, or by incineration, or by open burning, if allowed by state and local authorities. If burned, keep out of smoke.

For minor spills, leaks, etc., follow all precautions indicated on this label and clean up immediately. Take special care to avoid contamination of equipment and facilities during cleanup procedures and disposal of wastes. In the event of a major spill, fire, or other emergency, call 1-800-424-9300, day or night.

WARRANTY AND LIMITATION OF DAMAGES

Seller warrants that this material conforms to its chemical description and is reasonably fit for the purposes stated on the label when used in accordance with directions under normal conditions of use and **Buyer** assumes the risk of any use contrary to such directions. **Seller** makes no other express or implied warranty, including any other express or implied warranty of **Fitness** or of **Merchantability**, and no agent of **Seller** is authorized to do so except in writing with a specific reference to this warranty. In no event shall **Seller's** liability for any breach of warranty exceed the purchase price of the material as to which a claim is made.

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Caliber 90®, Concep®, Dual®, and Princep® trademarks of CIBA-GEIGY Corporation.
Bexton® trademark of DowElanco.
Gramoxone® and Sutan +® trademarks of ICI Americas.
Lasso®, Ramrod® and Roundup® trademarks of Monsanto Company.
CO-OP trademark of Universal Cooperatives, Inc.
UNIVERSAL COOPERATIVES, INC., MINNEAPOLIS, MN 55440

APPENDIX B

MSDS of Dursban®

Chemsico, Division of United Industries Corp.
P.O. Box 15842, St. Louis, MO 63114

Material Safety Data Sheet

Complies with OSHA's Hazard Communication Standard, 29 CFR 1910.1200

Hazardous Material Identification System-(HMIS)	
HEALTH - 2	REACTIVITY - 0
FLAMMABILITY - 2	PERSONAL - Rubber gloves, face mask or goggles

I Trade Name: Ace Dilutable Concentrate Dursban Insect Spray

Product Type: Liquid Dilutable Concentrate Insecticide

EPA Registration Number	Manufacturer	Emergency Telephone No.
33955-547-9688	Chemsico 8494 Chapin Industrial Drive St. Louis, MO 63114	For Chemical Emergency: 1-800-633-2873 For Information: 1-800-332-5553 Prepared by: H.L. Pauls Date Prepared: January 25, 1996

II Hazardous Ingredients/Identity Information

Chemical	%	OSHA PEL	ACGIH TLV
Xylene CAS #1330-20-7	89	100 ppm	100 ppm (skin)
Chlorpyrifos CAS #2921-88-2	6.62	0.2 mg/m³ (skin)	0.2 mg/m³ (skin)

III Physical and Chemical Characteristics

Appearance and Odor: Clear straw colored liquid. Chlorpyrifos odor.
Boiling Point: 285°F
Melting Point: NA
Vapor Pressure: NA
Specific Gravity: 0.88 (H_2O=1)
Vapor Density: greater than 1 (Air=1)
% Volatile (by vol.): 90%
Solubility in Water: emulsifies in water
Evaporation Rate: less than 1 (Butyl Acetate=1)

IV Fire and Explosion Hazard Data

Flash Point: 85°F (TCC)
Flame Extension: N/A
Flammable Limits: N/A
Autoignition Temp.: N/A
Fire Extinguishing Media: Water Fog, Carbon Dioxide, Dry Chemical
Decomposition Temp.: N/A
Special Fire-Fighting Procedures: Keep containers cool to avoid explosive ignition. Use self-contained breathing apparatus in enclosed area. Dike area to prevent runoff. Fight fire upwind.
Unusual Fire and Explosion Hazards: Vapors are heavier than air and may travel along ground to ignition sources distant from handling point. Vapors and fumes may be hazardous. Also see Section V.

V Reactivity Data

Stability: Stable
Polymerization: Will not occur
Conditions to Avoid: None.
Incompatible Materials: N/A
Hazardous Decomposition or Byproducts: Carbon dioxide, carbon monoxide, organic sulfides, hydrogen chloride.

VI Health Hazard Data

Ingestion (Swallowing): May be fatal if swallowed. First Aid: Call a physician or Poison Control Center. Do not induce vomiting because of possible aspiration hazard.
Skin Contact: May be injurious if absorbed through skin. First Aid: Remove contaminated clothing and immediately wash skin with plenty of soap and water.
Eye Contact: May be injurious to eyes. First Aid: Flush eyes with plenty of water and call a physician.
Inhalation Toxicity: Do not breathe vapors or spray mist. First Aid: Remove to fresh air if symptoms of cholinesterase inhibition appear and get medical attention.
Special Notes: Chlorpyrifos is a cholinesterase inhibitor. Treat symptomatically. Atropine only by injection is an antidote.
Health Conditions Aggravated by Exposure: None
Ingredients listed by NTP, OSHA or IARC as Carcinogens or potential carcinogens: None

VII Precautions for Safe Handling and Use

Steps to be Taken in Case Material is Released or Spilled:
Avoid breathing vapors. Remove ignition sources. Avoid skin contact with liquid. Soak up with absorbent material.
Waste Disposal:
Give to qualified waste disposal service.
Handling & Storage Precautions:
Do not store where temperatures can exceed 54°C (130°F).

VIII Control Measures

Read and follow label directions. They are your best guide to using this product effectively, and give necessary safety precautions to protect health.

IX Transportation Data

DOT Shipping Name - Consumer Commodity
DOT Hazard Class - ORM-D

The information and statements herein are believed to be reliable but are not to be construed as warranty or representation for which we assume legal responsibility. Users should undertake sufficient verification and testing to determine the suitability for their own particular purpose of any information or products referred to herein. NO WARRANTY OF FITNESS FOR A PARTICULAR PURPOSE IS MADE.

APPENDIX C

Illustration of Instruments

Illustration of Instruments

Instrument	Description
Wrist Action® Shaker	Burrel Model 75, Manufactured by Burrel Co., Pittsburgh, PA
Pressure Canister	NSF Testing Laboratory, Spartan NSDA-VS-01, max. wp. 130 psi (900Kpa), capacity 3 us gal (11.4 liter), The cornelius Co., Anoka, MI
Pressure Gauge	Testing Gause, Temperature compensated. 0.2psi subd., Accuracy Grade 3A, 0.25%, ASHCROFT®
Hydrostatic Head teste	Alfred Suter Co., Prel plaza Orangburg, NY
Thickness	Testing Machines, Inc., Amityville, NY
Air Permeability	No. 5138, Using Meriam Red oil- Sp. GR 0.827, each graduation equals 1/100 inches of water pressure, Fransier Precision Instrument Co. Inc. Gaithersburg, MD
High Performance Liquid Chromatography	Waters 712 WISP, 600E System Controller, 490 Programmable Multi wavelength Detector

VITA

Unchin Cho was born in Iri City, Chonbuk, Korea on October 27, 1969. She graduated from Iri Women's High School, Iri, Chonbuk, in 1987. She attended Chonbuk National University, Chonju, Korea, and in 1991, she graduated with a Bachelor of Engineering degree in Textile Engineering. She continued her graduate studies at the Chonbuk National University. At that time, she was awarded a Department Assistantship from the Department of Textile Engineering. In 1994, she received a Master of Engineering degree in Textile Engineering. In June of 1996, she began her graduate studies at the University of Tennessee, Knoxville in the United States. At that time, she was awarded a Research Assistantship from Agricultural Corn Growers. In August 1998, she received a Master of Science degree in Consumer and Industry Services Management.