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UNIVERSITY OF CALIFORNIA
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Rubber Latex Gloves as a Direct Dosimeter for Measuring Dermal Harvester Pesticide
Exposure Particularly With Malathion

A Thesis submitted in partial satisfaction
of the requirements for the degree of

Master of Science

in

Environmental Toxicology

by

Terry Enriquez Lopez

August 2011

Thesis Committee:

Dr. Robert Krieger, Co-Chairperson

Dr. David Eastmond, Co-Chairperson

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ABSTRACT OF THE THESIS

Rubber Latex Gloves as a Direct Dosimeter for Measuring Dermal Harvester Pesticide Exposure Particularly With Malathion

by

Terry Enriquez Lopez

Master of Science, Graduate Program in Environmental Toxicology
University of California, Riverside, August 2011
Dr. Robert Krieger, Co-Chairperson
Dr. David Eastmond, Co-Chairperson

Hands are an important route of dermal exposure to agricultural pesticides during strawberry harvesting. Direct dosimeters that trap pesticide residues as they contact workers during harvesting may be valuable sources for estimates of exposure. Latex gloves as hand dosimeters have been evaluated in two settings: 1) commercial strawberry farms, and, 2) controlled studies using a surrogate contact transfer device and malathion-treated turf.

With the assistance of field operators from a commercial strawberry farm, harvester glove samples were collected and obtained via overnight shipping for extraction and analysis of pesticide residues. Harvester gloves accumulated multiple pesticide residues during normal work periods (2 to 2.5 h). Thirteen different pesticide active ingredients were found on harvester gloves at different times. Pesticide residues can accumulate on rubber latex gloves up to ~20 mg/pair by intermittent contact during normal work.

To evaluate the accumulation of surface pesticide residues on light rubber latex gloves, a surrogate model system, the Brinkman Contact Transfer Unit (BCTU), was

developed. The BCTU consisted of latex gloves fitted on mannequin hands mounted in a wheeled chassis that could be pushed across a grid of treated turf. Using the BCTU on malathion-treated turf (2 lbs/A), residues accumulated on gloves (0.14–398 $\mu\text{g/glove}$) over a 13 d study period. Turf residues dissipated biphasically over 13 d and the malathion first-order half-life was 1.4 d. The percent transferred and recovered residue from treated turf to a gloved mannequin hand (assuming 420 cm^2 surface area) ranged from <1% to 10% based on measurements of deposition applied to turf. Concurrent applications of malathion and fenpropathrin (data not shown) to turf showed that gloves can accumulate multiple pesticide residues.

Transferable turf residues (TTRs) were also measured using the CDFA (California) roller and cotton cloth dosimeters. Residues accumulated on cotton cloths ranged from 0.002–0.117 $\mu\text{g}/\text{cm}^2$ for days 1 through 13. When PGRs ($\mu\text{g/glove}$) were plotted as a function of TTRs ($\mu\text{g}/\text{cm}^2$), a strong linear regression correlation was observed ($R^2 = 0.5\text{--}1.0$) and an empirical transfer factor of 1548 cm^2/glove was derived from the slope.

TABLE OF CONTENTS

CHAPTER 1: INTRODUCTION.....	1
1.1. CALIFORNIA STRAWBERRY AGRICULTURE.....	2
1.2. HARVESTER EXPOSURE ASSESSMENT.....	5
1.3. EFFECTIVE USE OF GLOVES IN FOOD SERVICE, HOSPITALS AND AGRICULTURAL SETTINGS.....	8
1.4. RUBBER LATEX GLOVES AS A DIRECT DOSIMETER.....	10
1.5. RESEARCH OBJECTIVES.....	11
1.6. REFERENCES.....	12
CHAPTER 2: MALATHION.....	16
2.1. INTRODUCTION.....	17
2.2. CHEMICAL IDENTIFICATION.....	18
2.3. ENVIRONMENTAL FATE AND TRANSPORT.....	19
2.4. TOXICOKINETICS.....	20
2.5. MECHANISMS OF ACTION.....	21
2.6. HEALTH EFFECTS AND TOXICITIES.....	22
2.7. ECOTOXICOLOGY.....	23
2.8. SUMMARY.....	24
2.9. REFERENCES.....	25
CHAPTER 3: PESTICIDE GLOVE RESIDUES ON A COMMERCIAL STRAWBERRY FARM.....	31
3.1. INTRODUCTION.....	32
3.2. RESEARCH OBJECTIVES.....	33

3.3. MATERIALS AND METHODS.....	33
3.4. RESULTS.....	38
3.5. DISCUSSION AND CONCLUSIONS.....	41
3.6. REFERENCES.....	44
CHAPTER 4: EVALUATION OF RUBBER LATEX GLOVES AS A DIRECT DOSIMETER.....	67
4.1. INTRODUCTION.....	68
4.2. RESEARCH OBJECTIVES.....	69
4.3. MATERIALS AND METHODS.....	69
4.4. RESULTS AND DISCUSSION.....	77
4.5. CONCLUSIONS.....	88
4.6. REFERENCES.....	92
CHAPTER 5: CONCLUSIONS.....	147

List of Tables

Table	Page
1.1. Target Populations [Workers] and Assumed Characteristics for Dermal Exposure Assessment.....	15
2.1. Types of Crops and Percent of Crops Treated With Malathion in 2009.....	26
2.2. Physical and Chemical Properties of Malathion.....	27
3.1 Pesticide Analytes Accumulated on Rubber Latex Gloves of Strawberry Harvesters.....	46
3.2. Results Of Multi-Residue Screens on Harvester Gloves From Ranch 1.....	47
3.3. Results Of Multi-Residue Screens on Harvester Gloves From Ranch 2.....	53
3.4. Survey of Malathion Glove Residues – Selected Application During 2010 Season.....	60
3.5. Survey of Captan Glove Residues – Selected Applications During 2010 Season.....	61
3.6. Survey of Fenpropathrin Glove Residues - Selected Applications During 2010 Season.....	62
4.1. Pilot Study Sampling Times and Environmental Conditions.....	94
4.2. Study 1 Sampling Times and Environmental Conditions.....	95
4.3. Study 2 Sampling Times and Environmental Conditions.....	96
4.4. Study 3 Sampling Times and Environmental Conditions.....	97
4.5. Study 4 Sampling Times and Environmental Conditions.....	98
4.6. Study Periods, Application Rates and Tank Mix Measurements.....	99
4.7. Method Validation and Recovery of Malathion.....	100
4.8. Recovery of Malathion From 1500 cm ² Cotton Cloth Dosimeters.....	101
4.9. Summary of Malathion Spray Deposition Results.....	102

4.10.	Tank Mix Analysis and Verification on GC.....	103
4.11.	Actual Percent of Spray Mix Deposited (Based on Analysis of Tank Mix).....	104
4.12.	Summary of Transferrable Turf Residues (TTRs).....	105
4.13.	Percent Recovered and Transferred Turf Residue (TTR) From Treated Turf to Cotton Cloth Dosimeters by CDFA Roller.....	106
4.14.	Malathion Half-lives From Pesticide Glove Residues (PGRs) and Transferable Turf Residues (TTRs) for Each Study Period.....	107
4.15.	Actual Glove Surface Area (cm ²) Contacting Turf Using Gloved Mannequin Hands.....	108
4.16.	Pilot Study Pesticide Glove Residues (PGRs).....	109
4.17.	Study 1 Pesticide Glove Residues.....	110
4.18.	Study 2 Pesticide Glove Residues.....	111
4.19.	Study 3 Pesticide Glove Residues.....	112
4.20.	Study 4 Pesticide Glove Residues.....	113
4.21.	Study Study 1 Normalized Pesticide Glove Residues.....	114
4.22.	Study 2 Normalized Pesticide Glove Residues.....	115
4.23.	Study 3 Normalized Pesticide Glove Residues.....	116
4.24.	Study 4 Normalized Pesticide Glove Residues.....	117
4.25.	Rainfastness Rating Chart: General Characteristics for Insecticide Chemical Classes.....	118
4.26.	Some of the Terminology Used for Adjuvants on Pesticide and Adjuvant Labels.....	119
4.27.	Activator 90® Classifications and Descriptions.....	119
4.28.	Study 1 Pesticide Glove Residues Expressed in µg/cm ²	120
4.29.	Study 2 Pesticide Glove Residues Expressed in µg/cm ²	121

4.30.	Study 3 Pesticide Glove Residues Expressed in $\mu\text{g}/\text{cm}^2$	122
4.31.	Study 4 Pesticide Glove Residues Expressed in $\mu\text{g}/\text{cm}^2$	123
4.32.	Study 1 Percent Malathion Residue Recovered and Transferred From Treated Turf To Latex Gloves.....	124
4.33.	Study 2 Percent Malathion Residue Recovered and Transferred From Treated Turf to Latex Gloves.....	125
4.34.	Study 3 Percent Malathion Residue Recovered and Transferred From Treated Turf to Latex Gloves.....	126
4.35.	Study 4 Percent Malathion Residue Recovered and Transferred From Treated Turf to Latex Gloves.....	127
4.36.	Transfer Factors in (cm^2/glove).....	128

List of Figures

Table	Page
1.1. Regression Line of Ratios Between Dermal Exposure Rates and Dislodgeable Foliar Residues of Various Pesticides and Crops.....	15
2.1. Chemical Structure of Malathion.....	28
2.2. Chemical Structure of Malaoxon.....	28
2.3. Proposed Biodegradation Pathway of Malathion in the Environment.....	29
2.4. Metabolic Pathways of Malathion in Animals	30
3.1. Highest Residues Found On Harvester Gloves Collected At Sites From Ranch 1.....	63
3.2. Highest Residues Found On Harvester Gloves Collected At Sites From Ranch 2.....	64
3.3. Selected Analyte Residues On Harvester Gloves From Ranch 1.....	65
3.4. Selected Analyte Residues On Harvester Gloves From Ranch 2.....	66
4.1. Measurements and Layout of Sampling Site for BCTU and CDFA Roller.....	129
4.2. Measurements and Layout of Deposition Coupons On a Turf Bay.....	130
4.3. Malathion Transferrable Turf Residues (TTRs) for Study 1.....	131
4.4. Malathion Transferrable Turf Residues for Study 2.....	132
4.5. Malathion Transferrable Turf Residues for Study 3.....	133
4.6. Malathion Transferrable Turf Residues for Study 4.....	134
4.7. Cotton Gloves Show Indicator Dye (Contact) on Fingers After “Run 1” Pass on Turf Using the BCTU.....	135
4.8. Cotton Gloves Show Indicator Dye (Contact) on Fingers After “Run 2” Pass on Turf Using the BCTU.....	136
4.9. Cotton Gloves Show Indicator Dye (Contact) on Fingers After “Run 3” Pass on Turf Using the BCTU.....	137

4.10.	Cotton Gloves Show Indicator Dye (Contact) on Fingers After “Run 4” Pass on Turf Using the BCTU.....	138
4.11.	Pesticide Glove Residues (PGRs) Plotted Against Post Application Days for Study 1.....	139
4.12.	Pesticide Glove Residues Plotted Against Post Application Days for Study 2...	140
4.13.	Pesticide Glove Residues Plotted Against Post Application Days for Study 3...	141
4.14.	Pesticide Glove Residues Plotted Against Post Application Days for Study 4...	142
4.15.	Malathion Pesticide Glove Residues (PGRs) Plotted Against Number of Runs From Each Study.....	143
4.16.	Percent Transferred Residue From Treated Turf to Gloves (Study 2).....	144
4.17.	Correlation of Residue Transfer (BCTU vs. CDFA Roller) Study 1.....	145
4.18.	Correlation of Residue Transfer (BCTU vs. CDFA Roller) Study 2.....	145
4.19.	Correlation of Residue Transfer (BCTU vs. CDFA Roller) Study 3.....	146
4.20.	Correlation of Residue Transfer (BCTU vs. CDFA Roller) Study 4.....	146

List of Appendices

1	Instruction Sheet Provided to DB Specialty Farms Field Operators.....	151
2	CDFA Roller Specifications and Experimental Protocol.....	152
3	The Brinkman Contact Transfer Unit (BCTU) Specifications and Experimental Protocol.....	153
4	Pictures of the Brinkman Contact Transfer Unit (BCTU).....	155
5	CDFA Roller Diagram and Picture.....	156
6	Malathion 8 Aquamul® Label.....	157
7	Malathion 8 Aquamul® MSDS.....	170
8	Activator 90® Label.....	173
9	Activator 90® MSDS.....	174
10	Spray Tracer Purple Label.....	177
11	Spray Tracer Purple MSDS.....	178

Abbreviations

Ag Ops: UC Riverside Agricultural Operations (Turfgrass Research Facility)

AI: Active Ingredient

ATSDR: Agency for Toxic Substances and Disease Registry

BCTU: Brinkman Contact Transfer Unit – a surrogate dermal monitoring system designed to measure contact transfer of surface pesticide residues from treated turf to gloved mannequin hands.

Cal/EPA: California Environmental Protection Agency

CDFA: California Department of Food and Agriculture

CDFA (California Roller): method to measure transferable chemical residue using a cotton cloth on a treated surface, covered with heavy paper, and pressed beneath a weighted roller

CDPR: California Department of Pesticide Regulation

CV: Coefficient of Variation

DFR: Dislodgeable Foliar Residue

FDA: Food and Drug Administration

FIFRA: Federal Insecticide, Fungicide, and Rodenticide Act

GC/FPD: Gas Chromatography/Flame Photometric Detector

GC/ECD: Gas Chromatography/Electron Capture Detector

GC/MS: Gas Chromatography/Mass Spectrometry

LC50: “Median Lethal Concentration”-concentration that is lethal to 50% of test organisms.

LD50: “Lethal Dose”-dose that is lethal to 50% of test organisms.

LLDPE: polyethylene-linear low density (Ziploc® bags)

LOAEL: Lowest Observed Adverse Effect Level

LOD: Limit of Detection

LOQ: Limit of Quantification

MSDS: Material Safety Data Sheet

NOAEL: No Observed Adverse Effect Level

OP: Organophosphorous insecticide

PCEP: Personal Chemical Exposure Program

PDD: Potential Dermal Dose

PDE: Potential Dermal Exposure

PGR: Pesticide Glove Residue

PHI: Pre-Harvest Interval

PPE: Personal Protective Equipment

REI: Restricted Entry Interval

RSD: Relative Standard Deviation

SD: Standard Deviation

TC: Transfer Coefficient

TSR: Transferable Surface Residue

TTR: Transferable Turf Residue

UC-IPM: University of California Integrated Pest Management

UCR: University of California, Riverside

USDA: United States Department of Agriculture

USEPA: United States Environmental Protection Agency

WPS: Worker Protection Standard

CHAPTER 1: INTRODUCTION

1.1. California Strawberry Agriculture

According to the 2007 Census of Agriculture, California is the leading agricultural producer in the United States (USDA, 2009). Nine out of the Nations' top 10 producing counties are located in the state of California. The state produces nearly half of all U.S.-grown fruits, nuts and vegetables. California's agricultural abundance includes more than 400 commodities with its top commodities being dairy products, grapes, almonds, lettuce and strawberries.

1.1.1. Production

California produces 89 percent of the total U.S. production of strawberries. In 2009, California produced 2.49 billion pounds valued at more than \$1.72 billion (DPR, 2010). California strawberry production occurs primarily along the central and southern coast, with smaller but significant production in the Central Valley.

1.1.2. Pests

California's moderate, Mediterranean climate, coupled with the State's fertile soil and diverse land resources, allows year-round production of many commodities including strawberries (CDFA, 2010). This environment also makes California a hospitable environment for invasive pests. The Lygus bug, *Lygus hesperus*, is the key insect pest of strawberries on the Central Coast, including the Watsonville and Santa Maria growing regions. Lygus bugs can cause a significant reduction in the yield and quality of the berries (Pickel et al., 1995). Lygus bugs are one of the causes of irregularly-shaped, cat-faced strawberries. They damage the berry by puncturing individual seeds which, in turn, stops development of the berry in the area surrounding the feeding site (UC-IPM, 2011).

Other major insect pests of California strawberries include the twospotted spider mite, cyclamen mite, aphids, root weevils, western flower thrips, cutworms, beet armyworm and whiteflies (CDPR, 2000).

1.1.3. Pesticide Use in California

To contain the loss of crops caused by pest attacks, most farmers rely on pesticide use as an effective means of plant and crop protection. The Department of Pesticide Regulation (DPR) reported that in 2009, nearly 156 million pounds of pesticides were applied statewide in California (DPR, 2010). The total acres treated with all pesticides on all California field crops were 64 million. For strawberry agriculture in California, a recorded total of 9,972,306 lbs AI were applied to 1,657,854 acres of strawberry fields. Most pesticides in California are applied at a rate of approximately 1 to 2 pounds per acre with the exception of fumigants which are applied at rates of hundreds of pounds per acre. Nearly 90% of the pounds of pesticide applied are pre-plant fumigants as part of IPM to control weeds, insects and plant disease.

Pesticide sales and use in the United States are regulated through labeling, registration and reporting as required by the Environmental Protection Agency (USEPA) through the Federal Insecticide, Fungicide and Rodenticide Act (USEPA, 1972).

1.1.4. Worker Exposure to Agricultural Pesticides and Safe Practices

In the 1950s, cases of organophosphate pesticide (OP) poisoning among field workers led to an interest in monitoring pesticide exposures (Maddy et al., 1990). Exposures resulting from pesticide use are usually benign with respect to safe levels established in well-planned safety evaluation studies and contemporary risk

characterization. However, the continual monitoring of pesticide exposures of workers is essential to address grower, registrant, regulatory, and public concerns about possible health effects of occupational exposures. There are two primary groups of field workers at risk of exposure to agricultural pesticides; handlers and harvesters. Handlers are persons who handle, mix, load or apply pesticide formulations. Handlers have the highest pesticide exposure potential but at the same time have the highest degree of protection from engineering controls and personal protective equipment (Krieger, 1995). Engineering controls include enclosed cabs, closed transfer systems, improved hose fittings and couplings, personal protective equipment (PPE) and formulations with low exposure potential. Such safety measure practices are performed to reduce the possibility of excessive exposures from concentrated pesticide formulations. Harvesters, on the other hand, lack the elaborate personal protective equipment of handlers. Harvesters' primary source of pesticide exposure is from dermal contact with plant surfaces where dislodgeable foliar residues (DFRs) of pesticides reside (Iwata et al., 1977). The primary means of minimizing harvester exposure is with the protection of work clothes and establishment of restricted entry intervals (REIs). Harvesters use their personal clothing in a manner that protects their face and mouth as well as general body with long sleeved shirts and long pants prior to entering treated fields. Restricted entry intervals (REIs), the period of time after a field is treated with a pesticide during which restrictions on entry are in effect, are set to safeguard field workers from contacting toxic levels of pesticide residues (CalEPA-DPR, 2007). REIs are established when the potential daily exposure to pesticide

residues may exceed safe levels (ARLA-PMRA, 2007). Potential daily exposures are based upon DFRs.

1.2. Harvester Exposure Assessment

The potential dermal dose (PDD) is defined as the amount of chemical that could be deposited on the skin during a given activity (EPA, 2007). In agriculture, workers are most commonly exposed to a pesticide agent by dermal contact with treated surfaces thereby dislodging the pesticide from the plant foliage making Dislodgeable Foliar Residues (DFRs) an important measurement in harvester exposure assessments (Iwata et al., 1977).

1.2.1. Dislodgeable Foliar Residues (DFRs)

Zweig et al. (1985) determined that dislodgeable foliar residues of pesticides consist of pesticide residues absorbed or adsorbed onto foliage. DFR is a chemical measurement of total surface foliar residue removed from a leaf surface using a dilute detergent (Gunther et al, 1973). Potential dermal exposure rates or PDEs were first approximated by Nigg et al. (1984) and Zweig et al. (1985) through the use of DFR measurements. From their studies, dermal exposure rate (mg/h) was plotted as function of DFR ($\mu\text{g}/\text{cm}^2$) (Figure 1.1). From the resulting slope, an empirical transfer coefficient (TC) of $5000 \text{ cm}^2/\text{h}$ was derived. Given DFR and time, the resulting Zweig-Poppendorf relationship to measure potential external dermal exposure (PDE) was developed (Zweig et al., 1985; Nigg et al., 1984):

$$\text{External Exposure (ug/person)} = \text{Dislodgeable Foliar Residues (DFR) (ug/cm}^2\text{)} \times \\ \text{Transfer Coefficient (cm}^2\text{/h)} \times \text{time (h)}$$

A universal transfer coefficient of 3000 $\mu\text{g}/\text{h}$ of dermal residues per $\mu\text{g}/\text{cm}^2$ foliar residues (based on a two-sided foliage surface) has been recognized for harvesters by the Department of Pesticide Regulation (DPR) (CalEPA-DPR, 2007). A transfer coefficient (TC) combined with the fraction of the amount of material applied (transferable residues from activity-related exposure data) constitutes the basis for dermal exposure assessment from treated foliage and surfaces (EPA, 2007).

1.2.2. Dosimetry

A number of methods have been assessed for the determination of potential worker exposure. Durham and Wolfe (1962) evaluated pesticide exposures using direct and indirect methods. “Direct” methods are those that involve trapping the chemical as it contacted workers during the work day (Li et al., 2011). Direct methods involve extracting and measuring pesticides from dosimeters such as external clothing, cotton gauze patches, or gloves. “Indirect” methods are those which provide indirect indication of potential for skin exposure. Such indirect methods include plant surface-sampling techniques and biological monitoring (Van Hemmen et al., 2006).

Dosimeters that measure dermal hand exposure are especially important to consider since hands are the part of the body that is in constant use in everyday activities and are the primary route of dermal exposure. Hands make up approximately 4-5% of the total body surface area, an average of 840 cm^2 (Table 1.1) for both males and females (USEPA, 2007). Cotton glove studies, recognized by the EPA, estimated that the glove residues from the cotton glove dosimeters represent 60-95% of the total external exposure. However, cotton glove dosimeters collected in the study do not represent an

appropriate transfer factor measurement of residue since these dosimeters have been found to overinflate actual residue exposure (Winterlin et al. 1984). Rubber latex gloves, often used by strawberry harvesters while contacting pesticide treated foliage, could be used as a direct dosimeter to assess external harvester exposure.

1.2.3. Transferable Surface Residues (TSRs)

Transferable Surface Residue (TSR), similar to DFR, is the amount of chemical that can be transferred from a surface to a dosimeter which can then be removed by extraction to yield the amount of transferred residue (Williams et al., 2002). A common and effective measure of TSR is estimated using the California (CDFA) roller. The CDFA roller, developed at the California Department of Food and Agriculture, is a standardized method of surrogate dermal monitoring for the determination of the potential transfer of pesticide residues from floor surfaces (Ross et al., 1991). The CDFA roller method utilizes a weighted cylinder that is rolled over a cloth dosimeter on a treated surface. In a study conducted by Welsh et al., (2005), the California roller was determined to be an effective technique for the measurement of transferable turf residue (TTR) and was shown to transfer an average of 2-3 times higher TTRs in a side-by-side comparison with another roller technique (Modified California Roller (MCR); (Fuller et al., 2001).

Hands are the primary route of exposure to agricultural pesticides by harvesters when contacting treated leaf surfaces (Krieger, 1995). An essential measure of TSR to account for hand exposures would be from direct methods such as hand dosimeters (gloves) (Li et al., 2011). Direct methods involve activity-related techniques which in the

case for harvesters, pesticide exposure is from hand contact with treated leaf surfaces as they pick crops. This involves pesticide accumulation on hands over time while contacting treated foliage. DFR, on the other hand, is a chemical measurement of total surface area removed from a leaf surface using a dilute detergent (Gunther et al, 1973), not a physical contact transfer that occurs under field conditions during harvest.

1.3. Effective Use of Gloves in Food Service, Hospitals and Agricultural Settings

Hands are the primary route of exposure for almost all daily activities. The use of some type of dermal hand protection is of critical importance in most “hands-on”, customer/consumer related occupations such as in public health professions and food service work. Glove use is common practice in these occupations because of the assumption that a physical barrier will prevent both the individuals and the product or patients from contaminants.

Food service establishments are provided with strict guidelines set by the USDA for the preparation and handling of food in order to prevent outbreaks of foodborne illnesses. Food handlers and poor handwashing practices have been determined as the source of most foodborne disease outbreaks (Monteville et al., 2001). Pether and Gilbert (1971) have determined that Salmonella bacteria can survive on the finger-tips for several hours at which time the hands can transmit infection. Food service workers are recommended to wear gloves while handling and preparing food. Studies conducted by Monteville et al. (2001) showed a 0.01% transfer was observed from food to hands and from hands to food when subjects wore gloves and a 10% transfer was observed without a glove barrier. Handwashing is often suggested to reduce microbial cross-contamination;

however, it does not eliminate it (Monteville et al., 2001). Combining handwashing and glove use may have an additive effect and further reduce the risk of cross-contamination from hands to food.

The use of gloves in hospital settings is a universal precaution that provides a barrier from the blood and body fluids of patients. The integrity and permeability of hospital gloves to bodily fluids is an important quality control concern that must be evaluated to ensure protection from bacterial pathogens. Permeability studies by DeGroot-Kosolcharoen and Jones (1989) of sterile and nonsterile latex and vinyl gloves to water, water with pressure and blood have shown that sterile latex gloves, often used for surgical procedures, exhibited the lowest leakage rates from all gloves tested with a range of 0-4%. Their study recognizes variables associated with leakage of gloves which in the case of nonsterile gloves (with leakage rates of 0-52% for latex and 0-32% for vinyl), packaging for nonsterile use was the main characteristic associated with the permeability to water or blood. Nonetheless, gloves can be regarded as a means to reduce soilage with body fluids (DeGroot-Kosolcharoen, et al., 1989). Additionally, medical personnel are advised to wash their hands immediately after removal of gloves.

Glove use by agricultural harvesters is variable and rarely required. In a 1999 survey of produce production practices, 93% of the farms that grew fruit and 89% that grew vegetables harvested the fruit or vegetable exclusively by hand (USDA, 2001). At DB Specialty Farms in Santa Maria, CA, rubber latex gloves are required by the grower as PPE for strawberry harvesters. Latex gloves as PPE first and foremost provide hand protection from environmental working conditions. For strawberry harvesters, this means

cosmetic protection of the skin by preventing the accumulation of dirt and juice on the hands. An additional benefit to glove use in agricultural settings is that gloves may be a food safety measure as observed in the food service industry. Hand contact with fruits and vegetables while harvesting and packaging may be important for food safety since there exists the potential for an infected worker to transfer microbial pathogens from hands to food. Transfer modes of microbial pathogens from workers may come in the form of sweat, blood, fecal matter or other body fluids. Just like glove use in hospital and food service establishments, gloves in agricultural settings are likely to reduce the transfer of microbial contaminants. Lastly, latex gloves are intended as a means of reducing pesticide exposure from treated foliage for each individual harvester since the primary route of exposure to agricultural pesticides is dermal. Although the possible benefits of glove use seem clear, there is little, if any objective evidence of their impact on safe work practices.

1.4. Rubber Latex Gloves as a Direct Dosimeter

Rubber latex gloves should be regarded as potential direct dosimeters for measuring dermal harvester pesticide exposures for a number of reasons: 1) they are the point of contact between the hand and foliage; 2) they have the potential of measuring multiple pesticide residues as harvesters come in contact with treated foliage; 3) gloves are non-invasive passive dosimeters that will not interfere with worker activity; and 4) they are overall a simple monitoring device. If residues are stable on the glove matrix, can be recovered by extraction methods and the results are reproducible under the same environmental conditions, then rubber latex gloves can be valuable direct dosimeters.

Hence, if rubber latex gloves are appropriate direct dosimeters, then they will be useful to measure external dose for harvester risk assessment to agricultural pesticides.

1.5. Research Objectives

The overall objective of this research was to evaluate the effectiveness and use of rubber latex gloves as a potential dosimeter for measuring dermal hand exposure as it relates to strawberry harvesters. To accomplish this, the following studies were conducted:

- 1) Harvester gloves, collected by field operators from a commercial strawberry farm (DB Specialty Farm in Santa Maria, CA), were collected and shipped via overnight shipping for extraction and analysis at the PCEP lab at UC Riverside. Spray records were also obtained and used for observations of residue dissipation.
- 2) A new surrogate system for dermal monitoring using rubber latex gloves as the dosimeter was developed and used in controlled studies utilizing turf at UC Riverside Turfgrass Research Facility. Additionally, the standardized method for dermal monitoring, the CDFA Roller, was also used to measure transferrable residue.

1.6. References

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Table 1.1: Target Populations [Workers] and Assumed Characteristics For Dermal Exposure Assessment (EPA, 2007)

EPA Office	Target population	Assumed characteristics		
		Age and sex	Body weight	Skin area/exposed skin area
OPPTS: Chem- STEER	Workers	Adults	70 kg (154 lb)	Total 18,150 cm ² (average of males and females); One hand, 420 cm ² ; two hands, 840 cm ²

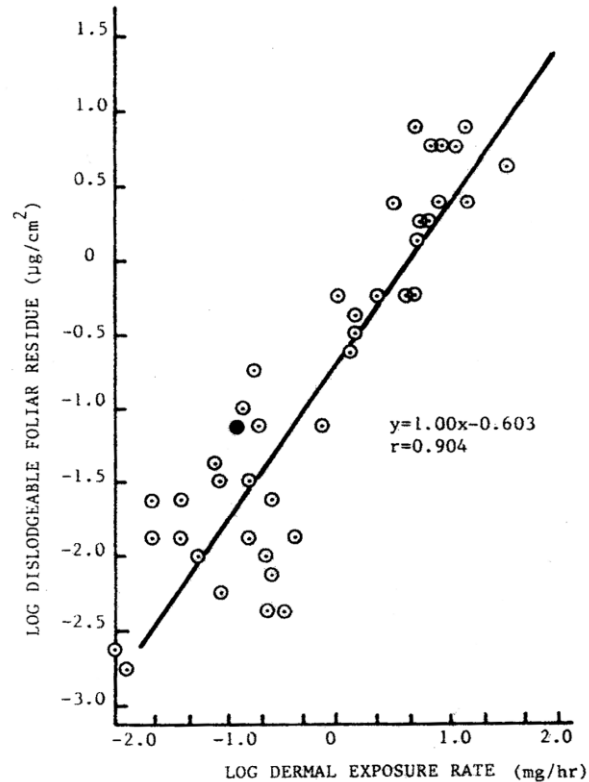


Figure 1.1: Regression Line of Ratios Between Dermal Exposure Rates and Dislodgeable Foliar Residues of Various Pesticides and Crops (Zweig et al., 1985)

CHAPTER 2: MALATHION

2.1. Introduction

Malathion is a broad-spectrum organophosphorous (OP) insecticide first produced in the United States in 1950 by American Cyanamid Chemical Company and registered in 1956 (ATSDR, 2003). Malathion has numerous uses in a variety of settings; agricultural, industrial, residential, governmental and pharmaceutical. Malathion controls a wide array of pests including fruit flies, lygus bugs, aphids, ticks, lice, moths and mites just to name a few. Regional pest eradication programs have utilized malathion for Boll Weevil eradication, Medfly control and mosquito control. In the pharmaceutical setting, malathion is used as a pediculicide for the treatment of head lice and their ova as regulated by the FDA (EPA, 2009). In 2009, The Department of Pesticide Regulation (DPR) reported that approximately 528,196 pounds of malathion (ai) were used in California for both agricultural and reportable non-agricultural applications (CDPR, 2009). In agriculture, approximately 276,308 acres were treated with malathion in 2009. For the majority of the agricultural sites for which malathion is registered and the Agency has use data, less than 1% of the crop is typically treated with malathion (EPA, 2009). However on several agricultural crops, for instance strawberries, malathion is applied to 10% of the crop or more (Table 2.1). For the strawberry field crop, 2009 pesticide use reports recorded that 149,924 pounds of malathion (ai) were applied to 76,413 acres of strawberry fields in California (CDPR, 2009). Due to an increase in lygus bug populations in the South Coast growing areas and widespread resistance to pyrethroid pesticides, there has been an increased use of malathion (up to 29 percent) on strawberry farms.

2.2. Chemical Identification

Malathion (O, O-dimethyl phosphorodithioate of diethyl mercaptosuccinate or Diethyl 2-[(dimethoxyphosphorothioyl)sulfanyl]butanedioate; CAS No. 121-75-5) is an insecticide that does not occur naturally (Figure 2.1). Pure malathion is a colorless liquid and technical-grade malathion, which contains >90% malathion and impurities in a solvent, is a brownish-yellow or amber liquid with a mercaptan or garlic odor. Malaoxon (Figure 2.2) is an oxygen analogue of malathion and can be found either as an impurity in malathion product or can be formed during the oxidation of malathion in air or soil (Newhart, 2006). Malaoxon is the active cholinesterase inhibiting metabolite of malathion. Malathion is formulated as an emulsifiable concentrate (EC), a dust (D), a wettable powder (WP), a ready-to-use (RTU) liquid, and a pressurized liquid (ATSDR, 2003). With a water solubility of 145 mg/L (Table 2.2), malathion is soluble in water and is readily soluble in most alcohols, esters, aromatic solvents, and ketones. It is only slightly soluble in aliphatic hydrocarbons (EPA, 2009). Malathion has a molecular weight of 330.36 g/mol with a density of 1.23 g/ml (Table 2.2). Henry's law constant for malathion is 4.89×10^{-9} atm-m³/mol (Table 2.2) indicating a low potential for volatilization from either moist soil or water. The vapor pressure of malathion is 3.38×10^{-6} mm Hg (Table 2.2) indicating a low potential for volatilization of the compound from dry soil surfaces (ATSDR, 2003). Malathion is stable at room temperature. However, it may decompose to form isomalathion if heated, a carboxyesterase inhibitor, as indicated by the MSDS (Appendix 7).

2.3. Environmental Fate and Transport

Malathion released into the environment can be transformed into an array of biological and environmental products (Figure 2.3). Malathion can undergo indirect photolysis to form its active cholinesterase inhibiting metabolite malaoxon by oxidation with photochemically produced hydroxyl radicals (ATSDR, 2003). The stability and degradation of malathion in the environment is dependent on the environmental conditions. Malathion has been observed to be unstable under alkaline conditions and increasingly stable under acidic conditions (EPA, 2009).

In soil, malathion dissipates by microbial mediated soil metabolism resulting in the formation of malathion β -monoacid (MMA), the major metabolite in soil (Newhart, 2006). Malathion half-life values on soil range from several hours to nearly 11 days (EPA, 2009). Malathion generally does not adsorb to soil and sediment. In addition, due to a high water solubility (145 mg/L), malathion is reportedly moderately to highly mobile in soils leading to a high potential for transport into surface and groundwater (ATSDR, 2003).

Hydrolysis is the primary degradation process of malathion in surface waters and occurs more rapidly at alkaline pHs (ATSDR, 2003). The half-life of malathion in surface water under aerobic conditions is 0.2 weeks at pH 8 and 21 weeks at pH 6 (Newhart, 2006). Malathion is not persistent under anaerobic conditions.

Malathion and malaoxon can be transported through air by drift of application spray, volatilization, fog and wind (Newhart, 2006). The occurrence of malathion in the atmosphere is generally localized. However, malathion has been detected in the fog of

remote pristine areas, indicating that long-range transport may occur under some conditions (ATSDR, 2003).

On plant surfaces, malathion half-lives range from <0.3-8.7 days (Newhart, 2006). Malathion metabolites in plants can be detected in new stem and leaf growth up to one-year post application (Newhart, 2006). The metabolites identified included malaoxon, isomalathion, diethyl maleate, monoethyl maleate, diethyl mercaptosuccinate, malathion dicarboxylic acid (MDCA), malathion mono-carboxylic acid (MMCA), diethyl methylthiosuccinate, diethyl fumarate, desmethyl malathion, and tetraethyl dithiodisuccinate (Jensen and Whatling, 2010).

2.4. Toxicokinetics

By oral route of administration, malathion is rapidly absorbed, biotransformed, and then quickly eliminated from the body. Malathion is absorbed in the intestine after ingestion with a half-life of absorption of 34 minutes (ATSDR, 2003). In a case study conducted by Morgade and Barquet (1982), malathion has been found in the spleen, adipose tissue, kidney, and brain but not in the liver. Elimination is via excretion mainly in urine (85-89%) and to some extent in feces (4-15%) primarily as mono- and dicarboxylic acids of malathion (Jensen and Whatling, 2010; Rodriguez et al., 1997).

Dermal exposure to malathion consequently leads to immediate absorption as a result of high capacity of the skin and the affinity of the plasma proteins for malathion (Menczel et al., 1983). Dermal absorption is the primary route of exposure to malathion following applications to fields and residential use (ATSDR, 2003). On skin, malathion has a relatively slow absorption rate half-life of 130 minutes (ATSDR, 2003). Saleh et al.

(1997) showed that by electronic autoradiography, 28% of the total recorded radioactivity (representative of malathion) was at the application site and 29% was distributed over the remaining skin (applied dose). Other areas with significant distribution after absorption were the small intestine (23%), large intestine (10%), and liver (5.4%). Excretion of malathion is primarily in urine by malathion urinary metabolites.

2.5. Mechanisms of Action

A proposed metabolic pathway for malathion in humans has been determined using animal models (Figure 2.4). The hydrolysis of the carboxylester moiety of malathion by tissue (possibly liver) or by plasma carboxylesterases resulting in α - and β -MMCA or MDCA are the major pathways of metabolism (Jensen and Whatling, 2010). It is postulated that the malaoxon is formed by oxidative desulfuration of malathion by hepatic microsomal enzymes and malaoxon is further metabolized by phosphatases. Hydrolysis by phosphatases would yield *O,O*-dimethyl phosphorothioic acid (from malaoxon) and *O,O*-dimethyl phosphorodithioic acid (from malathion).

Malaoxon is the toxic form of malathion that causes insecticidal activity (anti-AChE). Cohen (1984) and Matolczy (1988) determined that insects exhibit a deficiency in detoxifying carboxylesterases upon exposure to malathion thus allowing malathion to undergo oxidation to form malaoxon. In addition, Cohen (1984) noted that the mode of phosphorothionate insecticide activation was accomplished upon the conversion of thionate (P=S), an ineffective inhibitor of AChE, to oxon (P=O), a potent inhibitor of AChE, by monooxygenases.

2.6. Health Effects and Toxicities

Signs and symptoms of malathion intoxication are due to the effects of the metabolite, malaoxon, on the central and peripheral nervous system. Malaoxon inhibits acetylcholinesterase (AChE) thus preventing hydrolysis of the neurotransmitter acetylcholine. Continuous presence of acetylcholine at parasympathetic autonomic muscarinic receptors results in ocular effects (miosis, blurred vision), gastrointestinal effects (nausea, vomiting, abdominal cramps, diarrhea), respiratory effects (excessive bronchial secretions, chest tightness, bronchoconstriction), cardiovascular effects (bradycardia, decreased blood pressure), effects on exocrine glands (increased salivation, lacrimation), and effects on the bladder (incontinence). At the neuromuscular junction, excess acetylcholine will induce muscle fasciculations, cramps, diminished tendon reflexes, muscle weakness in peripheral and respiratory muscles, ataxia, and paralysis. Finally, overstimulation of brain cholinergic receptors will lead to drowsiness, lethargy, fatigue, headache, generalized weakness, dyspnea, convulsions, and cyanosis. (ATSDR, 2003).

Malathion has a low acute toxicity by oral, dermal and inhalation routes falling within the pesticide toxicity category of III or IV (EPA, 2009). In one study evaluated by the U.S. EPA, the acute oral LD₅₀ in rats was 5400 mg/kg/BW in male rats and 5700 mg/kg/BW in female rats (EPA, 2009). The acute dermal LD₅₀ in both male and female rats was >2000 mg/kg/BW. The acute inhalation toxicity in rats resulted in LC₅₀ > 5.2 mg/L (EPA, 2009). Short term oral toxicity studies conducted in rats, specifically a 28-day dietary study with dose levels ranging from 50 to 20,000 ppm, showed a NOAEL of 500

ppm (34.4 mg/kg/BW/day) for RBC cholinesterase inhibition (Jensen and Whatling, 2010). Dermal toxicity of malathion was examined in two 21-day toxicity studies using the rabbit where the NOAEL was 50 and 100 mg/kg BW/day based on inhibition of RBC cholinesterase (Jensen and Whatling, 2010). Two inhalation toxicity studies (14 days and 13 weeks) conducted on rats resulted in a NOAEL of 0.1 mg/kg BW/day based on cholinesterase inhibition (Jensen and Whatling, 2010).

Malathion is classified as having “suggestive evidence of carcinogenicity”. A quantitative cancer dose-response assessment is not indicated for pesticides in the “suggestive” category (EPA, 2009).

2.7. Ecotoxicology

Malathion can affect aquatic habitat and species due to its high potential to drift from ultra-low volume (ULV) applications (Newhart, 2006). In fish, malathion toxicity varies by species and ranges from highly toxic ($<0.1 \mu\text{g/l}$) to virtually non-toxic ($>100 \mu\text{g/l}$). LC₅₀ values for fish ranged from 4-11,700 $\mu\text{g/l}$ and 0.5-3,000 $\mu\text{g/l}$ based on 96-hour toxicity studies (Newhart, 2006). Bullfrogs exposed to malathion in water showed a decrease in survival at levels of 2,500 $\mu\text{g/l}$ or higher (Newhart, 2006).

In birds, malathion toxicity levels range from low to moderate levels in acute and subacute exposure (EPA, 2009). The LC₅₀ value of malathion for avian species was determined as 2639 mg/kg following acute exposure (EPA, 2009). Repeated exposure is of greater concern since malathion is non-persistent in the environment (Newhart, 2006).

2.8. Summary

Overall, malathion is a nonsystemic insecticide of low mammalian toxicity with contact, stomach and respiratory action. It has been found to be less persistent in the environment than other organophosphorous pesticides. Malathion undergoes metabolic activation to form malaoxon, which enhances toxicity by the inhibition of cholinesterase enzymes in blood, brain and nervous tissue throughout the body. Malathion does not cause permanent nerve damage. The small amount of malaoxon formed and rapid metabolism by detoxifying enzymes results in low mammalian toxicity.

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Table 2.1: Types of Crops and Percent of Crops Treated With Malathion in 2009

<i>Percent Crop Treated Range</i>	<i>Crops</i>
>10	blueberries, raspberries, strawberries, limes, cotton, cherries, greens, celery.
5-10	okra, walnuts, lettuce, avocados, onions, carrots, squash, asparagus, cantaloupes, cabbage, collards, kale.
1-5	alfalfa, pecans, wheat, rice, oranges, almonds, corn, peaches, apples, pears, tomatoes, potatoes, sorghum, grapes, beets, lemons, broccoli, cucumbers, grapefruit, pumpkins, sunflowers, watermelons, peas, corn, beans, peppers, plums, prunes, spinach, apricots, cauliflower.
<1	Approximately 54 crops make up this category, but are not listed here.

Reference: (EPA, 2009)

Table 2.2: Physical and Chemical Properties of Malathion

Common name	Malathion
CAS Registry Number	121-75-5
Empirical formula	C ₁₀ H ₁₉ O ₆ PS ₂
Chemical class	Organophosphate
CAS Nomenclature	Diethyl[(dimethoxyphosphinothioyl)thio]butanedioate
Molecular weight	330.36 g/mol
Color	Colorless liquid (pure form)/Deep brown to yellow
Physical state	Liquid
Odor	Garlic-like/Mercaptan
Melting point	2.9°C
Boiling point	156-157°C
Boiling point pressure	0.7 torr
Density at 25°C	1.23 g/cm ³
Solubility at 20°C	145 mg/L
Log K _{ow}	2.36
Vapor pressure at 30°C	3.38 x 10 ⁻⁶
Henry's Law Constant	4.89x10 ⁻⁹ atm-m ³ /mol
Flash Point	163°C

Reference: Compilation of references derived from ATSDR, 2003.

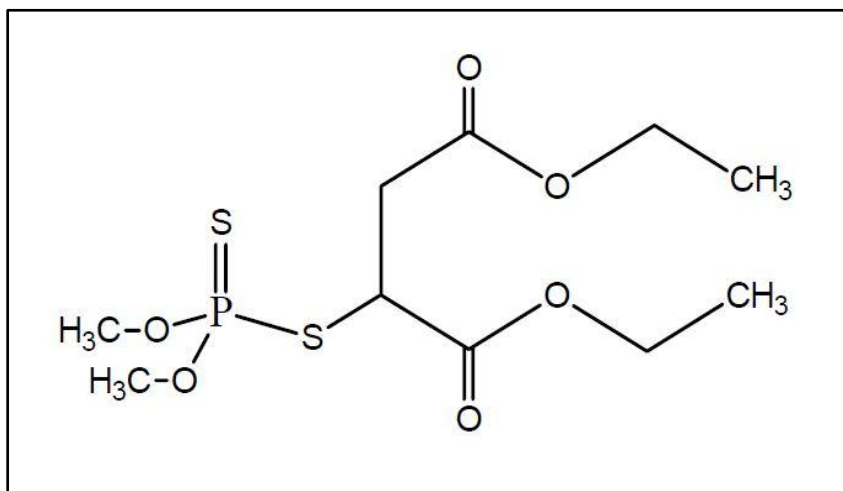


Figure 2.1: Chemical Structure of Malathion

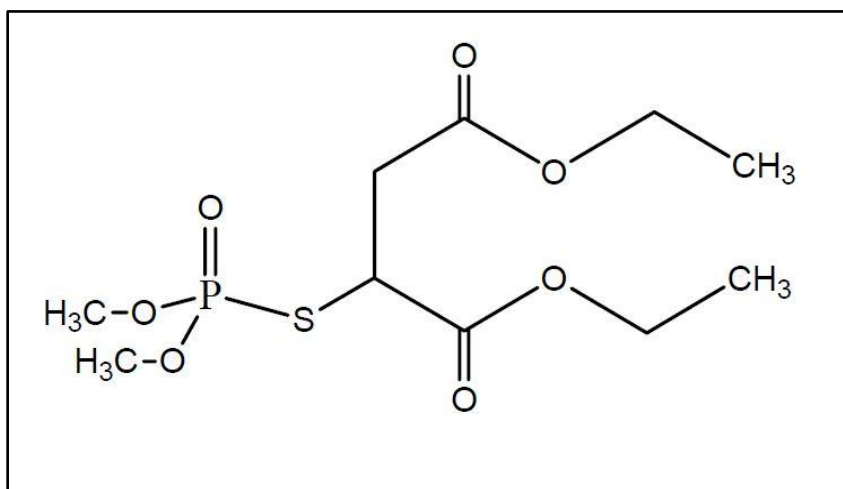


Figure 2.2: Chemical Structure of Malaoxon

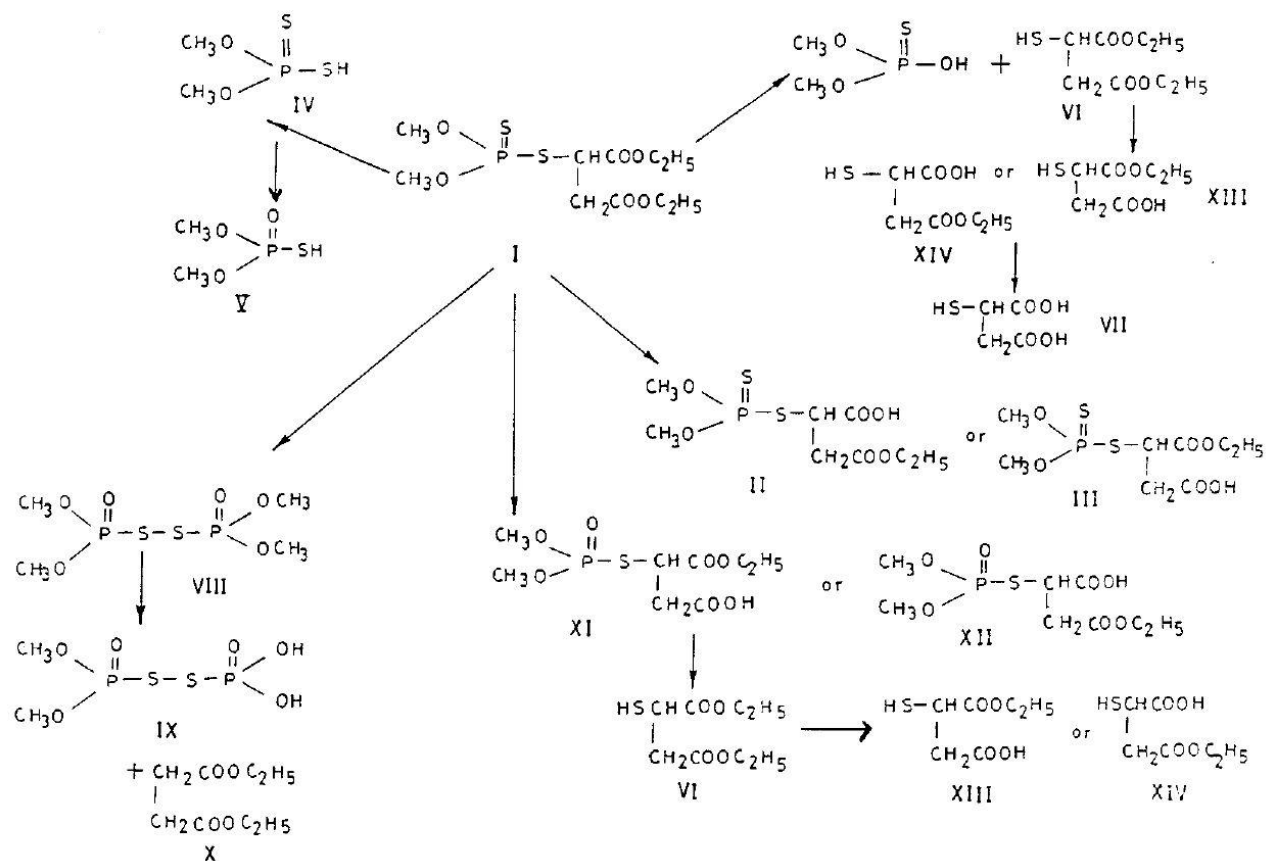


Figure 2.3: Proposed Biodegradation Pathway of Malathion in the Environment (Kaur, *et al.*, 1997)

(I) Malathion; (II) α – monoacid; (III) β – monoacid; (IV) *O,O*-dimethylphosphorodithioate; (V) *O,O*-dimethylphosphorothioic acid; (VI) diethylmercaptosuccinate; (VII) mercaptosuccinic acid; (VIII) bis-(dimethoxy phosphinothionyl sulphide); (IX) bis-(*O*-methoxy-*O*-hydroxy phosphinothionyl) sulphide; (X) diethylsuccinate; (XI) α – monoacid (malaoxon); (XII) β – monoacid (malaoxon); (XIII) ethyl mercapto α -succinate; (XIV) ethyl mercapto β -succinate

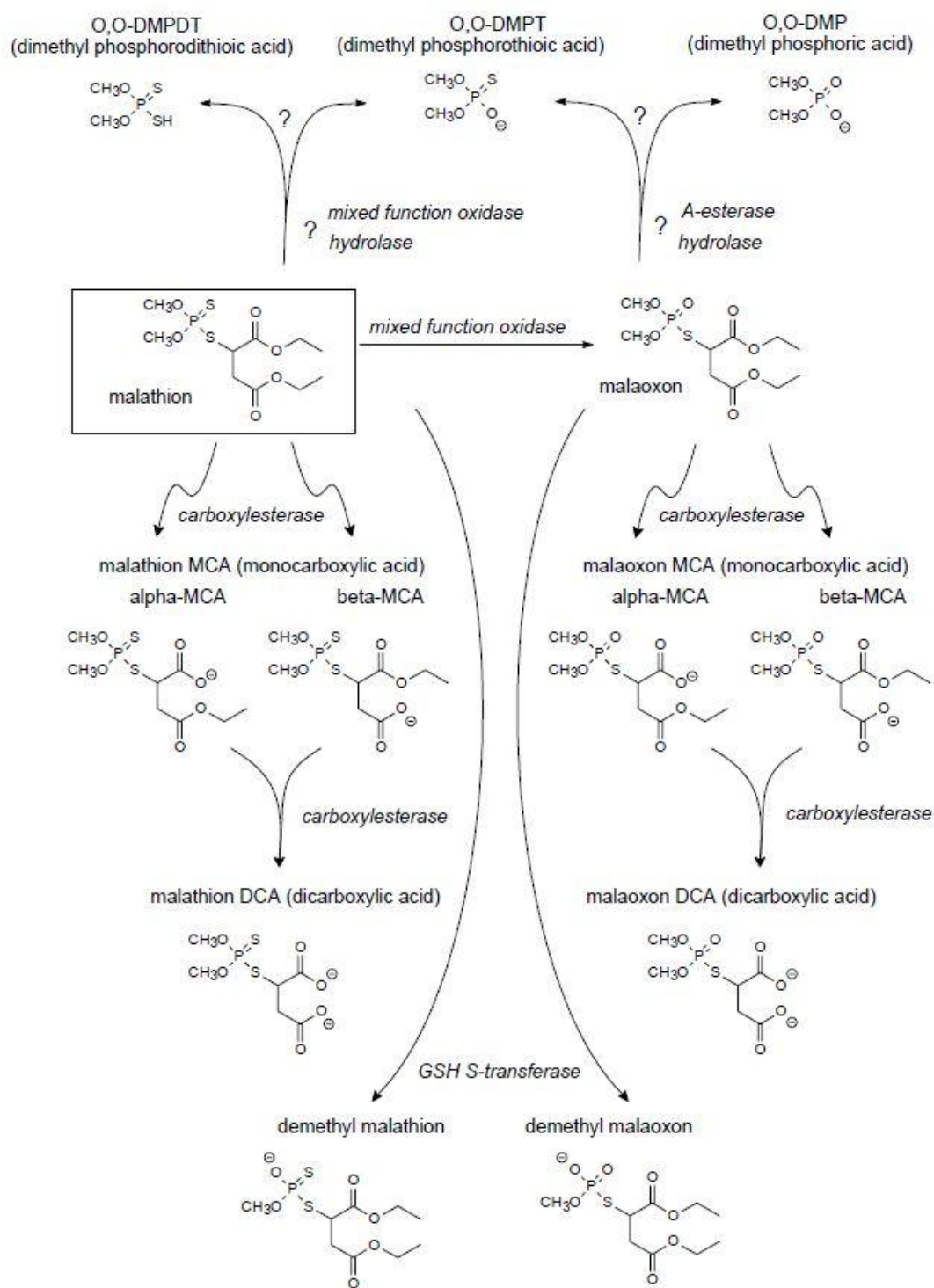


Figure 2.4: Metabolic Pathways of Malathion in Animals (ATSDR, 2003)

CHAPTER 3: PESTICIDE GLOVE RESIDUES ON A COMMERCIAL STRAWBERRY FARM

3.1. Introduction

Pesticides are critical components of integrated pest management in the production of flavorful and nutritious California strawberries. Pesticide use practices are highly regulated. Only products registered with the state of California and the U. S. Environmental Protection Agency can legally be used in integrated pest management. Harvester exposures to residual fungicides, insecticides, and miticides are continuing regulatory and health concerns. Harvester exposure to agricultural pesticides is largely by dermal hand contact to treated leaf surfaces during hand harvesting. To protect field workers from excessive exposure to pesticides after an application to the field, restricted entry intervals (REIs) go into effect. The REI is the period of time after a field is treated with a pesticide during which restrictions on entry are in effect to protect workers from potential exposure to hazardous levels of pesticide residues (CDPR, 2007). In addition, pre-harvest intervals, the period between the application of a pesticide and harvest, are established to ensure the crop will meet the established pesticide residue tolerances and protect the public from possible exposure to excessive residues (CDPR, www.cdpr.ca.gov/docs/enforce/compend/vol_8/chapter1.pdf).

Strawberry harvesting generally includes 8 h work shifts with breaks every 2 to 2.5 h after applicable REIs and PHIs following pesticide applications. Worker Protection Standard (WPS), a federal regulation designed to protect agricultural workers and pesticide handlers from pesticide-related illness, injury and exposure, requires all workers to complete a pesticide safety training prior to starting field work (EPA, 2005). WPS indicates the use of extensive PPE for handlers (including coveralls, gloves, and

respirators). However PPE, such as gloves, is not required for harvesters. During picking, harvesters commonly are seen wearing long-sleeved shirts, long pants, socks, shoes as required by WPS and gloves (variable usage) as well as for personal cosmetic protection from environmental exposures (i.e. sun, dirt, strawberry juice etc.).

3.1.1. Harvester Exposure

Hands are an important route of dermal exposure to agricultural pesticides during strawberry harvesting (Krieger et al., 1991). They are the direct point of contact to treated leaf surfaces during hand picking. EPA estimates that pesticide residues from cotton glove dosimeters represent 60-95% of the total external exposure to harvesters (unpublished observations). Evaluating hand dosimeters, such as latex gloves (required PPE at DB Specialty Farms in Santa Maria, CA), could be a valuable measure of external harvester exposure to agricultural pesticides.

3.2. Research Objectives

The purpose of this study was to evaluate the performance of latex gloves as dosimeters in a commercial strawberry farm setting. With the assistance and special collaborations made with DB Specialty Farms in Santa Maria California, harvester glove samples and spray records were obtained via overnight shipping. Rubber latex gloves were sampled to determine the accumulation of multiple pesticide residues. In addition, selected pesticide applications coupled with the spray records were studied to evaluate the dissipation of the pesticide residues as they behave in the field.

3.3. Materials and Methods

3.3.1. Sampling Preparation

To prepare a sampling collection, a set of 10 new quart-sized Ziploc® bags were properly labeled and placed in a gallon-sized Ziploc® bag. Each quart-sized bag was designated for the collection of a single pair of gloves. A collection of samples occurred on a single day of harvesting. A total of 7 collections were prepared for each Study (1.5 months). Glove samples were collected from two ranches within DB Specialty Farms for two continuous Study periods. Samples were collected over the course of 3 months in 2009 for multiple pesticide residue analysis (Ranches 1 and 2) and 5 months in 2010 to monitor applications of malathion, captan and fenprothrin (Ranch 2). The Study sampling sets (consisted of 7 collections) were then placed in an insulated box with Blue Ice pack (propylene glycol) along with detailed instructions for sample collection (Appendix 1). The insulated box and materials were transported to DB Specialty Farms in Santa Maria, CA via overnight shipping.

3.3.2. Field Sampling of Rubber Latex Gloves

Field sampling of rubber latex gloves was done by field operators at DB Specialty Farms. Instructions (Appendix 1) indicated that the date was to be recorded on the label of each collection bag. A total of 10 pairs of rubber latex glove samples were taken from 10 randomly selected harvesters at the lunch break (following a 2 to 2.5 h harvesting period) on a single day. This represented a glove collection. Collections were temporarily stored at DB Specialty Farms in a freezer (-20 °C). Periodically collections were placed in an ice chest containing frozen Blue Ice pack (propylene glycol) and shipped via overnight shipping to PCEP for extraction and analysis. Corresponding spray records were later obtained.

3.3.3. Sample Handling

Once samples arrived at the PCEP lab, an inventory entry was completed which included the date, time of arrival, temperature, number of glove samples and collections received. Samples were then immediately placed in an appropriately labeled bag and stored in the freezer at -20°C prior to extraction.

3.3.4. Sample Extraction and analysis

Prior to extraction, all glove samples were cut into small pieces using isopropyl alcohol-rinsed scissors. Using an online random number generator, 3 quart-sized Ziploc® bags, each containing a pair of gloves, were chosen from a collection (set of 10 pairs of gloves; section 3.3.1) and combined in a gallon-sized freezer bag to form 1 sample.

Quart-sized Ziploc® bags were saved and rinsed accordingly with solvent as indicated by each extraction method. All rinses were combined prior to shaking and extraction. Each gallon-sized bag containing the sample was double-bagged prior to adding extracting solvent. A total of 3 samples were obtained from each collection.

Three extracting methods using 1) 0.01% Surten solution 2) ethyl acetate, and 3) 3:7acetone-water solution, were evaluated to determine the most effective method for extracting pesticide residues from latex gloves. Using actual field samples from multi-residue screens (Tables 3.2 and 3.3), three collections from each ranch were chosen at random, extracted and analyzed by the 3 methods stated above. Best method was chosen on the basis of extraction efficiency, the number of analytes detected using that method, and simplicity and reproducibility (presented further in this chapter).

For method 1, 350 ml 0.01% Surten solution (evenly distributed) was added to the 3 saved quart-sized bags. Quart-sized bags were rinsed by hand shaking for 30 seconds and total volume was transferred to the gallon-sized Ziploc® containing the cut glove samples. Gallon-sized bags were shaken at high frequency on an Eberbach shaker for 20 minutes. This process was repeated two more times resulting in a final volume of 1050 mL. From the total final volume, 400 mL of solution were transferred to a separatory funnel for liquid:liquid extraction. Sodium chloride was added to facilitate the separation of the aqueous and organic layers. Methylene chloride (350 mL) was added and the separatory funnel was shaken by hand for 30 seconds. After the layers separated, the organic and aqueous layers were collected in Nalgene bottles. The process was repeated an additional 2 times: the second time with 350 mL methylene chloride and the third time with 300 mL methylene chloride. Sodium sulfate was added to the organic phase to remove residual water. The volume (1000 mL) was reduced using a Büchi rotary evaporator to about 5 mL. The remaining volume (5mL) was transferred to an 8 mL glass vial and reduced to dryness using a nitrogen evaporator. Acetone (2 mL) was added to the vials and vortexed. Samples were then ready for analysis.

For the method 2, pesticide residues were extracted from gloves by adding 300 mL of ethyl acetate (evenly distributed) to the 3 quart-sized glove storage bags. The bags were rinsed by hand shaking for 30 seconds and the total volume was transferred to the gallon-sized Ziploc® containing the cut glove samples. Samples were then shaken at high frequency for 20 minutes on an Eberbach shaker. The total extract was transferred to a round bottom flask and volume reduced to ~3-5 mL on a Büchi rotary evaporator.

Remaining volume was air-dried using light air flow. The Sample was re-suspended in 5 mL ethyl acetate and centrifuged prior to analysis. The Samples were stored in a freezer at -20°C.

Method 3 was identical to method 1 except that 400 mL of a 3:7 acetone-water solution was the rinsing solvent rather than the 0.01% Surten solution.

Method 2 using ethyl acetate as extracting solvent, yielded more pesticide residues from multi-residue screens than the 0.01% Surten or the 3:7 acetone-water solutions (Tables 3.2 and 3.3). Method 2 (using ethyl acetate) also yielded higher residue levels. The recoveries of spiked standards for method 2, the method of choice, are presented in Chapter 4.

For analysis of specific pesticides, 1 µL of sample extract was injected into a HP 5890 Gas Chromatograph equipped with Electron Capture Detector (GC/ECD) and a HP-5 capillary column 30 m lens x 0.25 mm x 0.25 mm x 0.25 µm film thickness. The instrumental limit of detection was 0.03 ppm.

GC/ECD Settings:

Injector temp: 220°C
Detector temp: 300°C
Initial Temp: 50°C, hold 1 minute
Ramp 1: 15°C/min to 190°C
Ramp 2: 10°C/min to 220°C
Ramp 3: 20°C/min to 280°C, hold for 13 min
Total Run Time: 29.33 min

For multi-residue screen analysis, sample extracts were appropriately labeled, wrapped in parafilm, packed in an insulated box with blue ice and shipped via overnight shipping to PrimusLabs.com, a commercial laboratory, for analysis. Sample extracts

were analyzed using the Luke (1981) method where residues are extracted by blending with acetone or water/acetone, then transferred from the filtered aqueous extract into organic solvent. The extract is cleaned up if necessary and analyzed on various gas chromatographs (GC). The equipment used by PrimusLabs.com is configured for the detection of organochlorines, organophosphates, organonitrates, organosulfates and N-methyl carbamates (PrimusLabs.com, 2010).

3.3.5. Data Analysis

Sample concentrations were calculated in Microsoft Excel using linear regression of a 5 point standard curve (linearity range: 1-50ppm GC-ECD). Means and standard deviations of data were calculated using Microsoft Excel. For multi-residue screens analyzed by PrimusLabs.com, the results are reported in parts per million (ppm) and calculated by volume ($\text{ppm } (\mu\text{g/ml}) \times 5 \text{ ml} = \mu\text{g/sample}$).

3.4. Results

Multi-residue screens from the 2009 season showed a total of 13 different analytes accumulated on rubber latex gloves (Table 3.1). Three of the analytes (naled, methomyl and propiconazole) specifically found only at Ranch 2, were recovered after extraction using 3:7 acetone-water mixtures and 0.01% Surten solutions (Tables 3.1 and 3.3). Residues ranged from non-quantifiable levels to up to 20 mg/pair over the 3 month sampling period (Figure 3.1). Eleven different residues were found on harvester gloves from Ranch 1 (150 A) where the highest residues of fenhexamid (5334 $\mu\text{g/pair}$) and the lowest residues of cyprodinil (43 $\mu\text{g/pair}$; Figure 3.1) were recorded. Multi-residue screens of gloves from the Ranch 2 showed accumulation of 13 different analytes with

the highest residue from captan at 20 mg/pair and lowest from methomyl at 4 µg/pair (Figure 3.2).

Using spray records and dates of sample collections, post application days were determined for Ranches 1 and 2 (Tables 3.2 and 3.3). Since gloves were collected randomly from 10 harvesters at the end of a work period, this practice may contribute to person-to person variability and complicate comparison of results from collection period to collection period. Dissipation of pesticide residues on strawberry plants could not be easily determined using glove residues (µg/pair).

From Ranch 1, four of the pesticide glove residues showed foliage dissipation over time (up to 34 days). They were azoxystrobin, bifenthrin, boscalid, and pyraclostrobin (Figure 3.3). However, apparent glove residues increased on subsequent collection days for each active ingredient at some time during monitoring. This unexpected pattern may be due to worker to worker sampling, the occurrence of moisture on gloves, or possibly uncertainties related to spray records, spray drift from an adjacent field or unrecorded pesticide applications.

Similarly, Ranch 2 showed no readily apparent distinguishable dissipation of foliage residues based upon pesticide glove residues (Figure 3.4). Selected residues (azoxystrobin, boscalid, captan and fenhexamid) from Ranch 2 shown in Figure 3.4, show the difficulties of using incomplete spray records and glove dosimetry. Captan, for example, spiked from 69 µg/pair on day 2 (post application) to 3000 µg/pair on day 17 without evidence of a spray event at the sampling site. Whether the discrepancy results from sampling or incomplete spray records cannot be determined.

Selected glove collections during the 2010 season were also evaluated for specific active ingredients (malathion, captan and fenpropathrin). Glove collections were selected within a 2 week time period of application of malathion, captan and fenpropathrin. Latex and nitrile gloves were analyzed separately. Nitrile gloves accumulated less pesticide residues than latex gloves (e.g. Table 3.5-captan Day 5: 1,363 µg/pair-nitrile < 7,651-8,481 µg/pair-latex) from all glove collections of the selected applications of malathion, captan and fenpropathrin (Tables 3.4, 3.5 and 3.6). There was no significant difference (P-value = 0.135) between nitrile and latex gloves for malathion residue levels. However, there is a significant difference between nitrile and latex gloves for captan and fenpropathrin levels with p-values of 0.038 and 0.035 at a 5% level of significance.

From malathion selected glove collections, the control sample (prior to application day) showed low levels of residual malathion residue (mean: 3 µg/pair) on harvester gloves (Table 3.4). After application of malathion (day 0), a spike in residues on gloves was observed on Day 8 (mean of 370 µg/pair–day 3 to 507 µg/pair–day 8). Data was compared with Li (2009) results where malathion applied at a rate of 1 lb/A resulted in mean glove residues values of 1000 µg/pair–day 4, 259 µg/pair–day 8 and 244 µg/pair–day 12. When the logarithm of glove residue from both studies was plotted as a function of sample day the resulting half-life for malathion was 3.6 d ($R^2=0.6$).

Captan showed a high accumulation of residue on rubber latex gloves on all days in the cycle within the 2010 season. Average captan glove residues ranged from 853 µg/pair to 12,365 µg/pair (Table 3.5) during the 2-2.5 h test periods. Captan glove residue levels were relatively higher than observed malathion and fenpropathrin residues.

When fenpropathrin records were matched with available spray records, there were elevated residues found in samples prior to the known application (167 µg/pair and 148 µg/pair: Table 3.6). There was no record of a previous fenpropathrin application at that glove collection site. High residue levels of fenpropathrin (1,964 µg/pair) were found on gloves on day 3 after the application (day 0). Subsequent glove collections with average fenpropathrin residues of 982 µg/pair occurred on a spray date (day 0) of which the source of the residue is likely from an adjacent site (adjacent to site of spray application) within the same Ranch (Ranch 2). An increase in fenpropathrin residues was seen on day 3 post application (982 µg/pair-day 0 to 1090 µg/pair-day 3). Whether this resulted from a mistaken spray record or a random sampling error is not known.

3.5. Discussion and Conclusions

Overall, rubber latex gloves have been found to accumulate multiple pesticide residues during normal harvesting periods (2 to 2.5 h) at a commercial strawberry farm. A total of 13 different pesticide parent compounds have been found on harvester gloves at different times (Table 3.1). Pesticide residues can accumulate on rubber latex gloves up to ~20 mg/pair (captan: 19,946.49 µg/pair) by intermittent contact during 2 to 2.5 h work periods.

Previous harvester exposure studies performed in 1981 by the University of California, Berkeley - Richmond Field Station (U.S. EPA, 1980-1986) used cotton gloves and cotton pad dosimeters to measure harvester exposure to agricultural pesticides. The total average pesticide residues in these studies ranged from 0.02 to 39 mg/h overall where hands accounted for 60% to 90% of the total dermal exposure. These studies

demonstrated the importance of hands for strawberry harvesters as the predominant route of exposure to agricultural pesticides. Additionally, the pesticide active ingredients (AIs) found on the hands and forearms of strawberry harvesters in these studies included captan, carbaryl, vinclozolin, and benomyl (U.S. EPA, 1980-1986; Li, 2009) demonstrating the usefulness of gloves to collect multiple residues.

In previous studies by Li et al. (2011), pesticide residues on gloves worn by strawberry harvesters declined biphasically over time. The half-lives were 2.7 days for malathion and 3.5 days for fenpropathrin during the initial 18 days of the study period (Li, et al., 2011). Additionally, Li et al. (2011) determined that gloves accumulate more fenpropathrin than malathion residues during concurrent monitoring of the two insecticides at the same application rate (1 lb/A). Similar observations are shown in this thesis where malathion applied at a rate of 2 lbs/A and fenpropathrin at 1 lb/A, resulted in fenpropathrin residue levels to be approximately 1 order of magnitude greater than malathion during the 2010 season (i.e. malathion day 4 accumulated 370 µg/pair mean glove residues whereas fenpropathrin day 3 accumulated 1,964 µg/pair; Tables 3.4 and 3.6). Accumulation of pesticide residues on gloves may be a useful dosimeter for harvester exposure measurements for residues on leaf surfaces.

The results of these glove residue studies were much more inconsistent than expected. Lacking actual field residue measurements or biomonitoring data, spray records were the only source of data available to evaluate the dissipation of residues. Uncertainties that could weaken the linkage between spray records and glove accumulation include, sampling errors (wrong bag/label/time), sample site identification,

uniformity of spray applications, presence or absence of moisture¹ in the field or on gloves, and unusual participant work or glove-handling practices and unrecorded or incomplete spray events. It is also important to note that pesticide applications were not necessarily uniform throughout an entire Ranch. Sites may have been selectively sprayed within a Ranch resulting in uneven glove accumulation of residues. Spray records do not provide specific spray/site data, therefore correlating spray records with specific glove dosimeters may limit the value of off-site sampling which may have resulted in some of the variability observed here.

¹ Results from Li et al., (2011) indicate that afternoon perspiration may also influence relative accumulation of residue on gloves (Li et al., 2011; Zhang, 2005).

3.6. References

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Table 3.1: Pesticide Analytes Accumulated on Rubber Latex Gloves of Strawberry Harvesters

Product	Active Ingredient
Abound	Azoxystrobin
Brigade	Bifenthrin
Captan	Captan
Danitol	Fenpropathrin
Dibrom	Naled [*]
Elevate	Fenhexamid
Lannate	Methomyl [*]
Malathion	Malathion
Orbit	Propiconazole [*]
Pristine	Pyraclostrobin/Boscalid
Quintec	Quinoxifen/Quinoline
Savey	Hexythiazox
Switch	Cyprodinil/Fludioxonil

All analytes were recovered from rubber latex gloves of strawberry harvesters at different times (during the 2009 and 2010 season) using the ethyl acetate solvent extraction method (method 2).

^{*}Analytes recovered from rubber latex gloves when extracted using 3:7 acetone-water or 0.01% Surten solutions.

Table 3.2: Results of Multi-Residue Screens on Harvester Gloves From Ranch 1

Active Ingredients (Product)	Study ^a	Collection ^b	Method ^c	Days ^d Post Application	Amounts ug/pair ^e
Azoxystrobin (Abound)	1	1	2	5	1893
		2	2	10	1980
		3	2	13	973
		4	2	17	N/D
		5*	1,2,3	20	N/D
		6	2	24	172
		7	2	2	849
	2	1	2	8	1335
		2*	1,2,3	11	N/D
		3	2	17	535
		4	2	21	234
		5*	2	25	283
		5*	1,3	25	N/D
		6	2	29	126
		7	2	32	152
Bifenthrin (Brigade)	1	1	2	N/R	N/D
		2	2	N/R	N/D
		3	2	N/R	N/D
		4	2	N/R	N/D
		5*	1,2,3	N/R	N/D
		6	2	N/R	N/D
		7	2	7	428
	2	1	2	13	423
		2*	2	16	120
		2*	1,3	16	N/D
		3	2	22	75
		4	2	26	N/D
		5*	2	30	54
		5*	1,3	30	N/D
		6	2	34	16
		1	2	N/R	N/D
		2	2	N/R	N/D
		3	2	N/R	N/D

Table 3.2 (cont.): Results of Multi-Residue Screens on Harvester Gloves From Ranch 1					
Active Ingredients (Product)	Study^a	Collection^b	Method^c	Days^d Post Application	Amounts ug/pair^e
Boscalid (Pristine)	1	4	2	N/R	N/D
		5*	1	2	139
		5*	2	2	211
		5*	3	2	432
		6	2	6	712
		7	2	15	313
	2	1	2	21	553
		2*	1	24	1
		2*	2	24	291
		2*	3	24	256
		3	2	3	1673
		4	2	7	N/D
		5*	2	11	906
		5*	3	11	938
		5*	2	11	1010
		6	2	15	536
		7	2	18	566
Captan	1	1	2	46	129
		2	2	51	N/D
		3	2	54	N/D
		4	2	58	247
		5*	1,2,3	61	N/D
		6	2	65	N/D
		7	2	74	607
	2	1	2	80	N/D
		2*	2	83	1
		2*	1,3	83	N/D
		3	2	89	N/D
		4	2	93	367
		5*	1,2,3	97	N/D
		6	2	101	N/D
		7	2	104	N/D
		1	2	11	N/D

Table 3.2 (cont.): Results of Multi-Residue Screens on Harvester Gloves From Ranch 1					
Active Ingredients (Product)	Study^a	Collection^b	Method^c	Days^d Post Application	Amounts ug/pair^e
Cyprodinil (Switch)	1	2	2	16	43
		3	2	19	N/D
		4	2	23	N/D
		5*	1,2,3	26	N/D
		6	2	30	N/D
		7	2	39	N/D
		1	2	45	N/D
	2	2*	1,2,3	48	N/D
		3	2	54	N/D
		4	2	58	N/D
		5*	1,2,3	62	N/D
		6	2	66	N/D
		7	2	69	N/D
Fenhexamid (Elevate)	1	1	2	46	N/D
		2	2	51	N/D
		3	2	54	N/D
		4	2	58	N/D
		5*	1	0	149
		5*	2	0	856
		5*	3	0	1511
		6	2	4	1428
		7	2	13	726
		1	2	19	751
	2	2*	1	22	26
		2*	2	22	277
		2*	3	22	323
		3	2	28	196
		4	2	32	222
		5*	1	2	754
		5*	2	2	5334
		5*	3	2	2809
		5*	2	2	190
		6	2	6	1126

Table 3.2 (cont.): Results of Multi-Residue Screens on Harvester Gloves From Ranch 1					
Active Ingredients (Product)	Study^a	Collection^b	Method^c	Days^d Post Application	Amounts ug/pair^e
		7	2	9	1389
Fenpropathrin (Danitol)	1	1	2	N/R	N/D
		2	2	N/R	N/D
		3	2	N/R	N/D
		4	2	N/R	N/D
		5*	1,2,3	N/R	N/D
		6	2	N/R	N/D
		7	2	N/R	N/D
	2	1	2	N/R	N/D
		2*	1,2,3	N/R	N/D
		3	2	N/R	N/D
		4	2	N/R	N/D
		5*	2	N/R	741
		5*	1,3	N/R	N/D
		6	2	N/R	168
		7	2	N/R	91
Hexathiaox (Savey)	1	1	2	11	N/D
		2	2	16	N/D
		3	2	19	525
		4	2	23	N/D
		5*	1,2,3	26	N/D
		6	2	30	N/D
		7	2	39	N/D
	2	1	2	45	N/D
		2*	1,2,3	48	N/D
		3	2	54	N/D
		4	2	58	N/D
		5*	1,2,3	62	N/D
		6	2	66	N/D
		7	2	69	N/D
		1	2	N/A	28
		2	2	N/A	54
		3	2	N/A	31

Table 3.2 (cont.): Results of Multi-Residue Screens on Harvester Gloves From Ranch 1					
Active Ingredients (Product)	Study^a	Collection^b	Method^c	Days^d Post Application	Amounts ug/pair^e
o-Phenyl phenol	1	4	2	N/A	3
		5*	1	N/A	135
		5*	2	N/A	34
		5*	3	N/A	148
		6	2	N/A	120
		7	2	N/A	67
	2	1	2	N/A	115
		2*	1	N/A	N/D
		2*	2	N/A	117
		2*	3	N/A	43
		3	2	N/A	62
		4	2	N/A	105
		5*	1	N/A	5
		5*	2	N/A	148
		5*	3	N/A	54
		5*	2	N/A	110
		6	2	N/A	87
		7	2	N/A	153
Pyraclostrobin (Pristine)	1	1	2	N/R	N/D
		2	2	N/R	N/D
		3	2	N/R	N/D
		4	2	N/R	N/D
		5*	1	2	N/D
		5*	2	2	54
		5*	3	2	41
		6	2	6	423
		7	2	15	37
	2	1	2	21	N/D
		2*	1,2,3	24	N/D
		3	2	3	1224
		5*	1	11	N/D
		5*	2	11	37
		5*	3	11	32

Table 3.2 (cont.): Results of Multi-Residue Screens on Harvester Gloves From Ranch 1					
Active Ingredients (Product)	Study^a	Collection^b	Method^c	Days^d Post Application	Amounts ug/pair^e
		5*	2	11	513
		6	2	15	87
		7	2	18	205
Quinoxifen (Quintec)	1	1	2	14	214
		2	2	19	143
		3	2	22	N/D
		4	2	26	42
		5*	1,2,3	29	N/D
		6	2	33	17
		7	2	42	11
	2	1	2	48	N/D
		2*	1,2,3	51	N/D
		3	2	57	N/D
		4	2	61	N/D
		5*	2	2	288
		5*	1,3	2	N/D
		6	2	6	159
		7	2	9	N/D

N/D represents non-detectable residues.

N/R represents no record available. Spray records were used to determine post application days.

^aA study consists of 7 collections which occurs over a period of 1.5 months. Studies 1 and 2 are continuous therefore spray applications and post application days can overlap.

^bA collection consists of 10 pairs of glove samples of which 3 pairs were selected, combined and analyzed as one sample (results shown in table as µg/pair).

^cThree extraction methods were used throughout the course of the study period which include: 1) 0.01% Surten solution 2) ethyl acetate 3) acetone:water solution.

^dPost application days are determined by spray records.

^eThree pairs of gloves (n=3) were selected, combined and analyzed as one sample (results shown in table as µg/pair). Calculated as follows: (µg/sample)/3 pairs = µg/pair.

*Collection samples analyzed by all 3 methods.

Table 3.3: Results of Multi-Residue Screens on Harvester Gloves From Ranch 2

Active Ingredients (Product)	Study ^a	Collection ^b	Method ^c	Days ^d Post Application	Amounts ug/pair ^e
Azoxystrobin (Abound)	1	1	2	N/R	N/D
		2	2	N/R	N/D
		3	2	N/R	N/D
		4	2	N/R	N/D
		5*	1,2,3	1	N/D
		6	2	5	31
		7*	1,2,3	6	N/D
	2	1	2	12	377
		2	2	1	264
		3	N/C	N/C	N/C
		4	2	7	1091
		5	2	13	572
		6	2	19	18
		7*	1,2,3	26	N/D
Bifenthrin (Brigade)	1	1	2	N/R	N/D
		2	2	N/R	59
		3	2	N/R	N/D
		4	2	N/R	N/D
		5*	1,2,3	N/R	N/D
		6	2	N/R	N/D
		7*	1,2,3	N/R	N/D
	2	1	2	N/R	N/D
		2	2	N/R	N/D
		3	N/C	N/C	N/C
		4	2	N/R	11
		5	2	N/R	N/D
		6	2	N/R	N/D
		7*	1,2,3	N/R	N/D
	1	1	2	85	N/D
		2	2	90	N/D
		3	2	93	72
		4	2	97	90
		5*	1	100	N/D
		5*	2	100	36

Table 3.3 (cont.): Results of Multi-Residue Screens on Harvester Gloves From Ranch 2					
Active Ingredients (Product)	Study^a	Collection^b	Method^c	Days^d Post Application	Amounts ug/pair^e
Boscalid (Pristine)		5*	3	100	33
		6	2	104	16
		7*	1	113	N/D
		7*	2	113	35
		7*	3	113	15
	2	1	2	119	73
		2	2	122	N/D
		3	N/C	N/C	N/C
		4	2	2	205
		5	2	8	24
		6	2	14	470
		7*	1	21	22
		7*	2	21	569
		7*	3	21	226
Captan (Captan)	1	1	2	1	949
		2	2	6	513
		3	2	9	349
		4	2	13	212
		5*	1	16	N/D
		5*	2	16	2657
		5*	3	16	1067
		6	2	2	69
		7*	1	11	N/D
		7*	2	11	19946
		7*	3	11	3538
	2	1	2	17	3001
		2	2	20	1238
		3	N/C	N/C	N/C
		4	2	26	501
		5	2	32	843
		6	2	38	N/D
		7*	1	45	N/D
		7*	2	45	148

Table 3.3 (cont.): Results of Multi-Residue Screens on Harvester Gloves From Ranch 2					
Active Ingredients (Product)	Study^a	Collection^b	Method^c	Days^d Post Application	Amounts ug/pair^e
		7*	3	45	56
Cyprodinil (Switch)	1	1	2	11	91
		2	2	16	36
		3	2	19	N/D
		4	2	23	N/D
		5*	1,2,3	26	N/D
		6	2	30	N/D
		7*	1,2,3	39	N/D
	2	1	2	45	N/D
		2	2	48	N/D
		3	N/C	N/C	N/C
		4	2	54	N/D
		5	2	60	N/D
		6	2	66	N/D
		7*	1,2,3	73	N/D
Fenhexamid (Elevate)	1	1	2	N/R	N/D
		2	2	N/R	N/D
		3	2	N/R	N/D
		4	2	N/R	N/D
		5*	1,2,3	N/R	N/D
		6	2	3	N/D
		7*	1	12	517
		7*	2	12	3029
		7*	3	12	1720
	2	1	2	18	1225
		2	2	21	392
		3	N/C	N/C	N/C
		4	2	27	214
		5	2	0	199
		6	2	6	2478
		7*	1	1	N/D
		7*	2	1	5802
		7*	3	1	2543

Table 3.3 (cont.): Results of Multi-Residue Screens on Harvester Gloves From Ranch 2					
Active Ingredients (Product)	Study^a	Collection^b	Method^c	Days^d Post Application	Amounts ug/pair^e
Fenpropathrin (Danitol)	1	1	2	19	N/D
		2	2	24	N/D
		3	2	27	N/D
		4	2	31	N/D
		5*	1,2,3	34	N/D
		6	2	38	305
		7*	1,3	47	N/D
		7*	2	47	60
	2	1	2	53	N/D
		2	2	56	N/D
		3	N/C	N/C	N/C
		4	2	0	N/D
		5	2	6	N/D
		6	2	12	219
		7*	1,2,3	19	N/D
Methomyl (Lannate)	1	1	2	N/R	N/D
		2	2	N/R	N/D
		3	2	N/R	N/D
		4	2	N/R	N/D
		5*	1,2,3	N/R	N/D
		6	2	3	N/D
		7*	1,2	12	N/D
		7*	3	12	4
	2	1	2	18	N/D
		2	2	21	N/D
		3	N/C	N/C	N/C
		4	2	27	N/D
		5	2	33	N/D
		6	2	39	N/D
		7*	1,2,3	46	N/D
		1	2	N/R	N/D
		2	2	N/R	N/D
		3	2	N/R	N/D

Table 3.3 (cont.): Results of Multi-Residue Screens on Harvester Gloves From Ranch 2					
Active Ingredients (Product)	Study^a	Collection^b	Method^c	Days^d Post Application	Amounts ug/pair^e
Naled (Dibrom)	1	4	2	N/R	N/D
		5*	1	1	33
		5*	2	1	N/D
		5*	3	1	9
		6	2	5	N/D
		7*	1,2,3	14	N/D
	2	1	2	0	N/D
		2	2	3	N/D
		3	N/C	N/C	N/C
		4	2	9	N/D
		5	2	15	N/D
		6	2	21	N/D
		7*	1,2,3	28	N/D
o-Phenyl phenol	1	1	2	N/A	2870
		2	2	N/A	4018
		3	2	N/A	1840
		4	2	N/A	812
		5*	1	N/A	N/D
		5*	2	N/A	60
		5*	3	N/A	42
		6	2	N/A	3262
		7*	2	N/A	65
		7*	3	N/A	31
		7*	1	N/A	56
	2	1	2	N/A	41
		2	2	N/A	63
		3	N/C	N/C	N/C
		4	2	N/A	59
		5	2	N/A	14
		6	2	N/A	59
		7*	1	N/A	7
		7*	2	N/A	N/D
		7*	3	N/A	16

Table 3.3 (cont.): Results of Multi-Residue Screens on Harvester Gloves From Ranch 2					
Active Ingredients (Product)	Study^a	Collection^b	Method^c	Days^d Post Application	Amounts ug/pair^e
Propiconazole (Orbit)	1	1	2	19	N/D
		2	2	24	N/D
		3	2	27	N/D
		4	2	2	N/D
		5*	1,2	5	N/D
		5*	3	5	22
		6	2	9	N/D
		7*	1,2,3	6	N/D
	2	1	2	12	N/D
		2	2	1	N/D
		3	N/C	N/C	N/C
		4	2	7	N/D
		5	2	13	N/D
		6	2	19	N/D
		7*	1,2,3	26	N/D
Pyraclostrobin (Pristine)	1	1	2	85	N/D
		2	2	90	48
		3	2	93	192
		4	2	97	384
		5*	1,2,3	100	N/D
		6	2	104	N/D
		7*	1,2,3	113	N/D
	2	1	2	119	41
		2	2	122	N/D
		3	N/C	N/C	N/C
		4	2	2	N/D
		5	2	8	N/D
		6	2	14	134
		7*	1	21	N/D
		7*	2	21	36
		7*	3	21	28
		1	2	5	41
		2	2	10	39

Table 3.3 (cont.): Results of Multi-Residue Screens on Harvester Gloves From Ranch 2					
Active Ingredients (Product)	Study^a	Collection^b	Method^c	Days^d Post Application	Amounts ug/pair^e
Quinoxifen (Quintec)	1	3	2	13	77
		4	2	17	88
		5*	1,3	20	N/D
		5*	2	20	148
		6	2	24	53
		7*	1,2,3	33	N/D
	2	1	2	39	N/D
		2	2	42	22
		3	N/C	N/C	N/C
		4	2	48	N/D
		5	2	0	N/D
		6	2	6	N/D
		7*	1,2,3	13	N/D

N/D represents non-detectable residues.

N/R represents no record available. Spray records were used to determine post application days.

N/C represents no collection. No samples were collected for Study 2 Collection 3.

^aA study consists of 7 collections which occurs over a period of 1.5 months. Studies 1 and 2 are continuous therefore spray applications and post application days can overlap.

^bA collection consists of 10 pairs of glove samples of which 3 pairs were selected, combined and analyzed as one sample (results shown in table as µg/pair).

^cThree extraction methods were used throughout the course of the study period which include: 1) 0.01% Surten solution 2) ethyl acetate 3) acetone:water solution.

^dPost application days are determined by spray records.

^eThree pairs of gloves (n=3) were selected, combined and analyzed as one sample (results shown in table as µg/pair). Calculated as follows: (µg/sample)/3 pairs = µg/pair.

*Collection samples analyzed by all 3 methods.

Table 3.4: Survey of Malathion Glove Residues – Selected Application During 2010 Season

Post Application Days	n ^a / # ^b	Glove Type	Residue (ug/sample)	Residue (ug/pair)	Mean Residue (ug/pair) ^c	S.D. ^d	C.V. ^e
-1	1/3	Nitrile	9	3	3	0	5
	1/3	Nitrile	9	3			
	1/3	Latex	10	3			
0* (2 lbs/A)	No Collection						
4	1/3	Nitrile	814	271	370	97	26
	1/3	Latex	1123	374			
	1/3	Latex	1395	465			
8	1/3	Latex	1783	594	507	76	15
	1/3	Latex	1392	464			
	1/3	Latex	1386	462			
12	1/3	Latex	180	60	70	24	34
	1/3	Latex	160	53			
	1/3	Latex	292	97			

*application day (day 0) and corresponding spray rate (lb/A). ^a number of samples. ^b number of pairs of gloves. ^c average of 3 samples from one collection day. ^d Standard Deviation. ^e Coefficient of Variation. There are insufficient data available to determine a half-life.

Table 3.5: Survey of Captan Glove Residues – Selected Applications During 2010 Season

Post Application Days	n ^a /# ^b	Glove Type	Residue (ug/sample)	Residue (ug/pair)	Mean Residue (ug/pair) ^c	S.D. ^d	C.V. ^e
0* (3 lbs/A)	No Collection						
1	1/3	Nitrile	13265	4422	6977	3326	48
	1/3	Nitrile	17318	5773			
	1/2	Latex	21475	10737			
0* (2.5 lbs/A)	1/3	Latex	13336	4445	3276	2099	64
	1/3	Latex	13589	4530			
	1/3	Nitrile	2559	853			
0* (3 lbs/A)	No Collection						
1	1/3	Latex	33272	11091	10658	1960	18
	1/3	Latex	37094	12365			
	1/3	Latex	25552	8518			
5	1/3	Latex	22953	7651	5832	3892	67
	1/3	Nitrile	4091	1364			
	1/2	Latex	16963	8481			
8	1/3	Nitrile	4989	1663	2025	705	35
	1/3	Nitrile	4725	1575			
	1/3	Latex	8513	2838			

*application day (day 0) and corresponding spray rate (lb/A). ^a number of samples. ^b number of pairs of gloves. ^c average of 3 samples from one collection day. ^d Standard Deviation. ^e Coefficient of Variation. There are insufficient data available to determine a half-life.

Table 3.6: Survey of Fenpropathrin Glove Residues - Selected Applications During 2010 Season

Post Application Days	n ^a /# ^b	Glove Type	Residue (ug/sample)	Residue (ug/pair)	Mean Residue (ug/pair) ^c	S.D. ^d	C.V. ^e
-4	1/3	Nitrile	430	143	167	41	25
	1/3	Nitrile	430	143			
	1/2	Latex	430	215			
-2	1/3	Latex	460	153	148	5	3
	1/3	Latex	439	146			
	1/3	Nitrile	432	144			
0* (1 lb/A)	No Collection						
3	1/3	Latex	33272	1694	1964	258	13
	1/3	Latex	37094	2208			
	1/3	Latex	25552	1990			
0* (1 lb/A)	1/3	Latex	22953	1201	982	430	44
	1/3	Nitrile	4090	487			
	1/2	Latex	16963	1257			
3	1/3	Nitrile	2928	976	1090	505	46
	1/3	Nitrile	1954	651			
	1/3	Latex	4926	1642			

*application day (day 0) and corresponding spray rate (lb/A). ^a number of samples. ^b number of pairs of gloves. ^c average of 3 samples from one collection day. ^dStandard Deviation. ^eCoefficient of Variation. There are insufficient data available to determine a half-life.

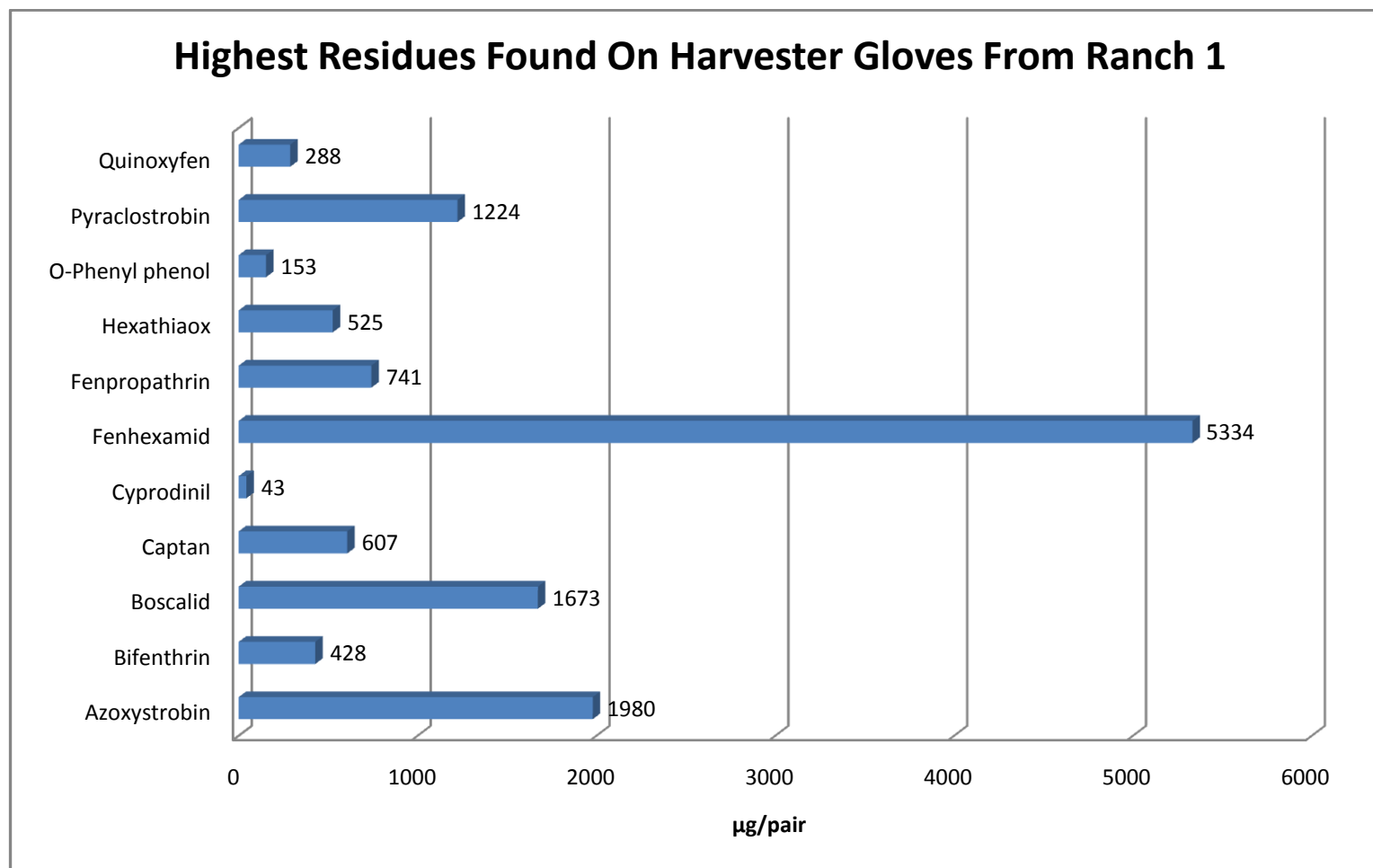


Figure 3.1: Highest Residues Found on Harvester Gloves Collected at Sites From Ranch 1

Highest residues (µg/pair) found on harvester gloves at any time during a 3 month monitoring period from Ranch 1 (Table 3.2).

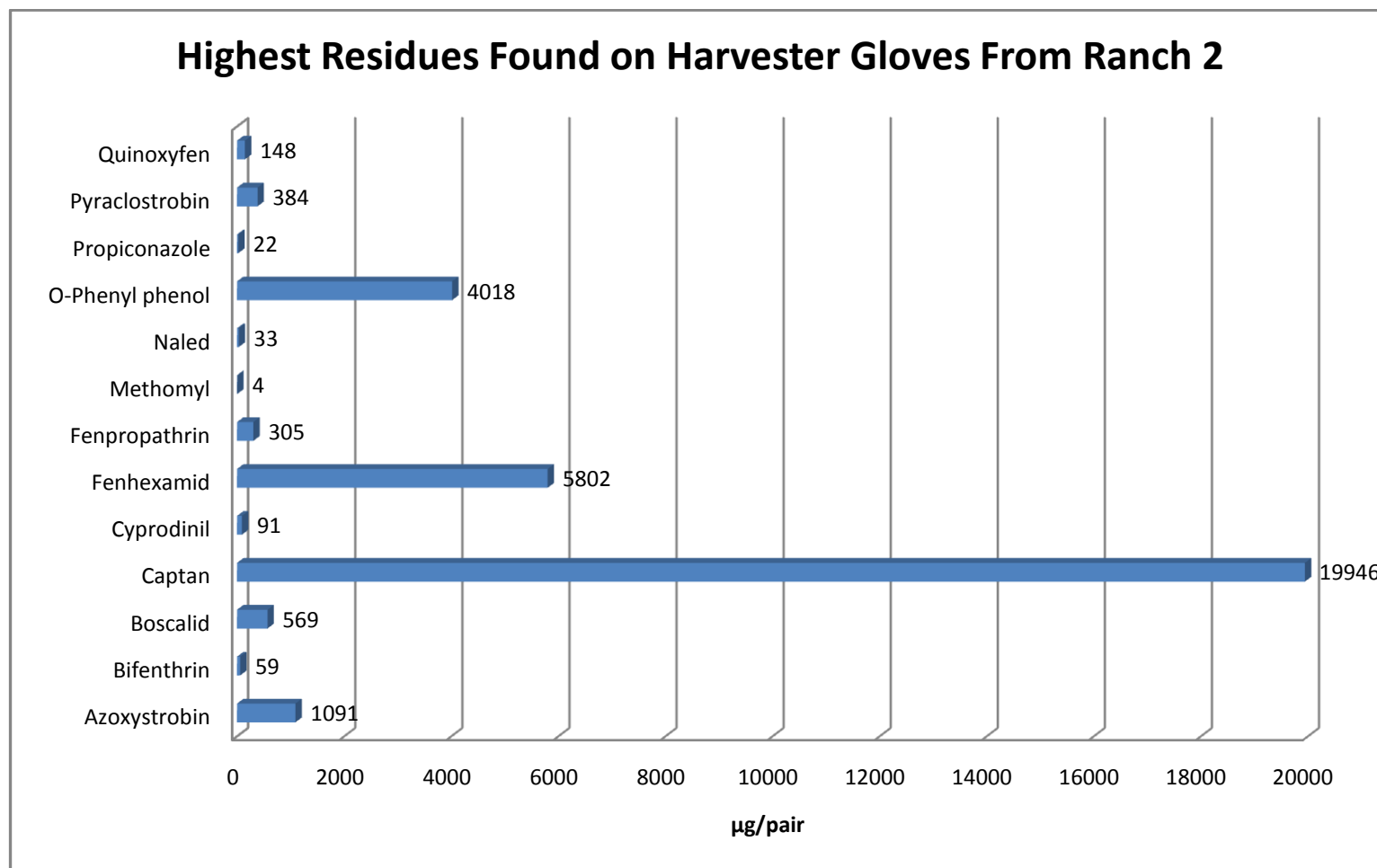


Figure 3.2: Highest Residues Found on Harvester Gloves Collected at Sites From Ranch 2

Highest residues (µg/pair) found on harvester gloves at any time during a 3 month monitoring period from Ranch 2 (Table 3.3).

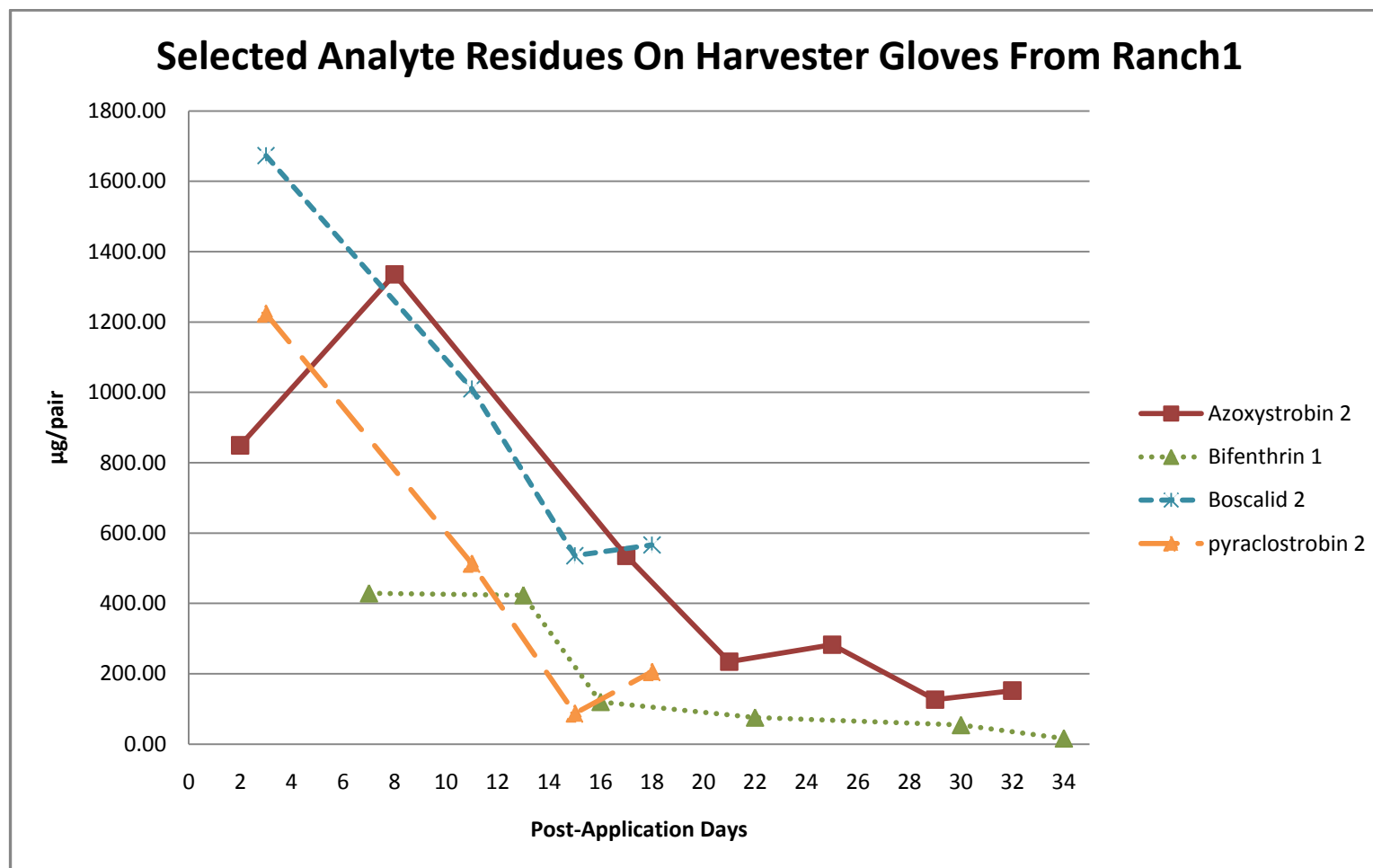


Figure 3.3: Selected Analyte Residues on Harvester Gloves From Ranch 1

Ethyl acetate-extracted analyte glove residues plotted µg/pair vs. post-application days (Table 3.2). These examples show the difficulties with the use of spray records and glove dosimeters. In the legend, numbers next to analyte correspond to a spray application.

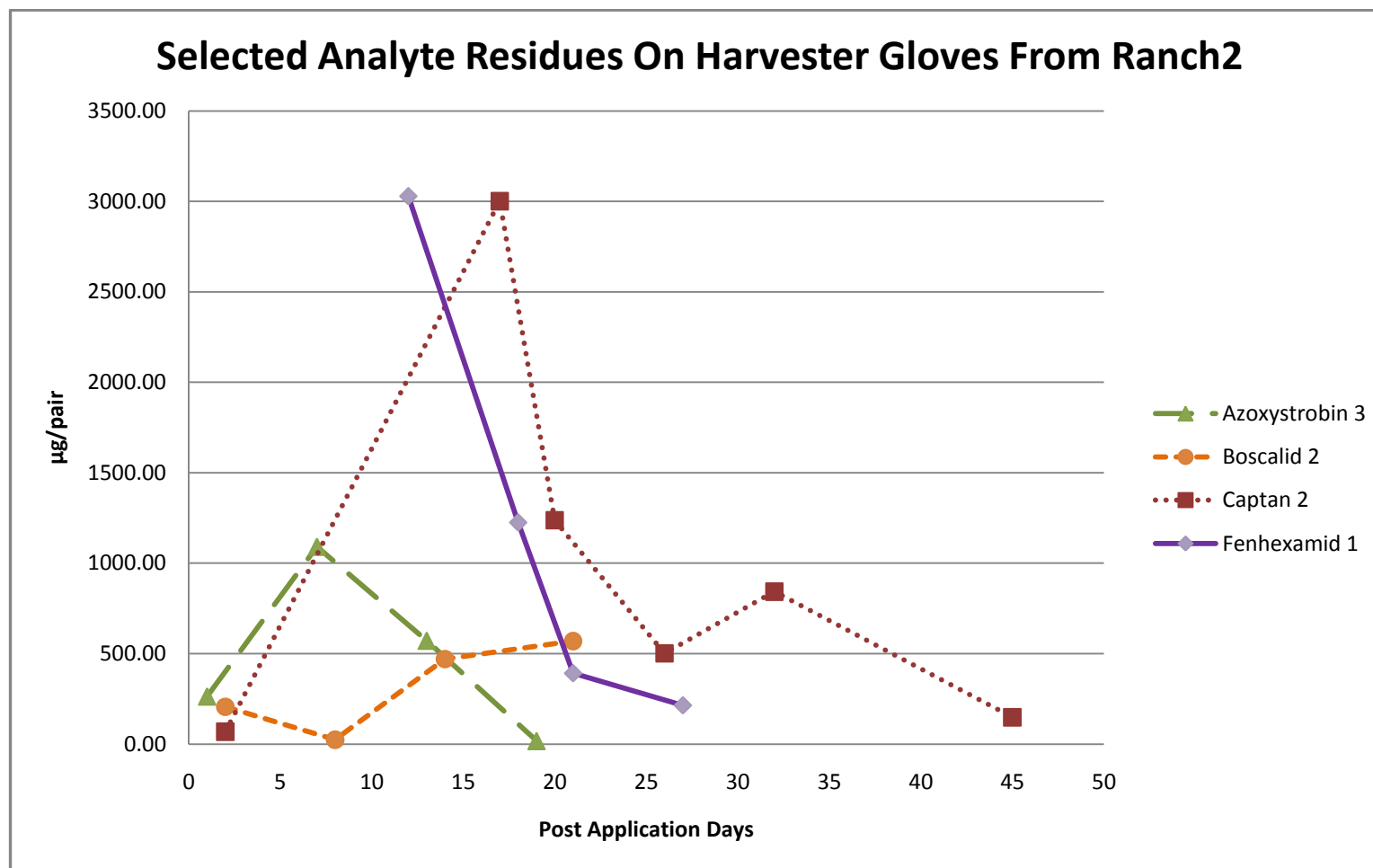


Figure 3.4: Selected Analyte Residues on Harvester Gloves From Ranch 2

Ethyl acetate-extracted analyte glove residues plotted µg/pair vs. post-application days (Table 3.3). These examples show the difficulties with the use of spray records and glove dosimeters. In the legend, numbers next to analyte correspond to a spray application.

CHAPTER 4: EVALUATION OF RUBBER LATEX GLOVES AS A DIRECT DOSIMETER

4.1. Introduction

Hands are the primary point of contact and dermal route of pesticide exposure of strawberry harvesters (Krieger et al., 1995). Previous field studies using light rubber latex gloves worn by harvesters for a 2 to 2.5 h periods showed accumulation of malathion residues ranging from 481 to 1670 $\mu\text{g}/\text{pair}$ ($n=10$) at the 3-day pre-harvest interval (PHI) where residues were the highest (Li et al., 2011). Those studies support the idea that light latex gloves might be used as direct dosimeters to indicate potential dermal harvester exposure. This research was done to measure the accumulation of malathion on rubber latex gloves under controlled conditions.

To evaluate the effectiveness of light rubber latex gloves as a dosimeter to measure harvester exposure to agricultural pesticides, a contact transfer system was developed. The sampling device permits time-dependent accumulation of surface residues from turf. This surrogate model system, now known as the Brinkman Contact Transfer Unit (BCTU) brings gloves into direct contact with treated turf as the BCTU is passed over predetermined lanes in measured “runs”. The BCTU would provide a measure of Pesticide Glove Residues (PGRs) from treated turf to assess transfer and accumulation of surface pesticide residues. In addition, since the CDFA roller has been extensively used and is the standardized method to sample transferable residue from floor surfaces (Williams et al., 2008) and turf (Bernard et al., 2001 and Welsh et al., 2005) for estimates of human exposure in risk characterization, it was also used in these studies. Turf was the foliar system for its simple maintenance, ease of access and availability.

4.2. Objectives

The primary objective of this study was to evaluate the use of rubber latex gloves as a direct dosimeter to measure contact-transfer of malathion to rubber latex gloves. Additionally, other environmental factors affecting residue transfer of pesticides from treated foliage to gloves were also evaluated including the effect of precipitation on rainfastness, presence of moisture and the use of an adjuvant in the tank mix.

4.3. Materials and Methods

4.3.1. Test and Reference Substances

Malathion (O, O-dimethyl phosphorodithioate of diethyl mercaptosuccinate; CAS No. 121-75-5) was applied to turf in aqueous sprays. The liquid formulation used was Malathion 8 Aquamul, organophosphate insecticide, EPA Registration No. 34704-474, manufactured for Loveland Products, Inc. (Greeley, CO.; Appendices 8 and 9). This test substance was stored in a secure storage facility at the UC Riverside Turfgrass Research Facility.

Malathion recovery studies were performed using standards purchased from Chem Service (P.O. Box 599, West Chester, PA. 19381). Purity of malathion standard used was 99.2%.

4.3.2. Test System and Materials

The test system consisted of tall fescue tall fescue (*Festuca arundinacea* Schreb. var. 'Bonzai') planted May 1993, 100% white cotton cloth, and Rite Aid® Multi-Purpose Sanitary Latex Medical Powder Free Gloves. Sampling of turf residues was done using

latex gloves and cotton cloths with the Brinkman Contact Transfer Unit (BCTU) and CDFA roller, respectively.

4.3.3. Test Site and Standard Operation

The test site was established within the UC Riverside Agricultural Operations (Ag Ops) Turfgrass Research Facility which allocated two turf plots identified as Bay 1 and Bay 2. The turf was tall fescue grass that was mowed to approximately 1.75 inches (44 mm) weekly prior to treatments. No mowing was done during data collection. The turf was healthy except for some dry patches near the roadside. Scheduled irrigation of the turf was performed on Sunday, Tuesday, Wednesday and Friday mornings, at approximately 0600. No irrigation was applied during field studies. Irrigation resumed immediately after each study. Irrigation was determined from the estimated crop evapotranspiration (ET_c) replacement divided by the irrigation system uniformity (DU) as calculated by California Irrigation Management Information System (CIMIS, 2009).

The sprays were applied in the morning, between 0900 and 1100. Excess moisture was recorded (Tables 4.1-4.5). Fenpropathrin was also applied as a tank mix at a rate of 2 lbs/A. A summary of results is presented in section 4.5.

4.3.4. Transferrable Turf Residues

4.3.4.1. *The Brinkman Contact Transfer Unit (BCTU)*

The Brinkman Contact Transfer Unit (BCTU) is intended to use gloved mannequin hands to collect surface pesticide residues from treated turf by contact transfer. The idea is that as strawberry harvesters pick berries, they run their gloved hands along treated foliage thereby accumulating surface pesticide residues as they work. The

BCTU was designed to mimic this specific worker activity and progressive passes over multiple lanes of turf represent harvester contact with treated foliage.

The BCTU is a modified cart (lawn mower chassis), fitted with three right-handed mannequin hands (Female Mannequin Hand-Jewelry Display D3; Mannequin Hub) attached within the cart (Appendix 4). The hands were labeled A, B, and C to designate their position. The mannequin hands are positioned to not drag as the cart is pushed across the turf. The mannequin hands were fitted with a clean single latex glove for each sampling (runs 1, 2, 3 or 4). See section 4.3.5 and Appendix 2.

4.3.4.2. CDFA Roller

CDFA roller was also used to measure transferable pesticide residues from turf. The CDFA roller used for the study was a 30 lb assembly that was rolled 20-times over a treated area of turf. The cotton cloth (1500 cm²) is the dosimeter of the assembly. One forward and one backward motion equals one roll. See section 4.3.5 and Appendix 3.

4.3.5. Experimental Design

The UC Riverside Turfgrass Research Facility allocated two turf plots identified as Bay 1 and Bay 2 measuring a total of ~5400 sq ft (507.1 m² or 0.05 ha) to conduct measurements of transferable turf residues. Each Bay was approximately 30' wide by 90' in length (Figure 4.1). The actual sampling area was a smaller rectangular area within (22.5' by 70') within each Bay. Approximately 10' from the end of each end (length) and 4' from each side (width) was not used for BCTU runs. An area of 10' x 6' at the end of the Bay was used for TTRs using the CDFA Roller. Each Bay was divided into six lanes of approximately 3.75' wide by 70' in length. Passing the BCTU up and down the length

of one lane represented one run. Two runs required the use of 2 lanes and three runs used 3 lanes and so forth. Each lane was used once in a run. The beginning and end of the lanes were marked with flags. Colored strings marked the lanes.

A total of four Studies plus a Pilot Study were conducted utilizing turf. Sprays were applied on day 0 and turf residues were sampled on days 1, 3, 5, 7, 9, 11, 13. No sampling was performed on days of heavy precipitation.

4.3.6. Equipment and Application Procedures

A licensed pest control applicator loaded, mixed and applied the aqueous sprays used for these studies. In the Pilot Study and Study 1, only applications of malathion were sprayed. In Studies 2, 3 and 4, tank mixes of malathion and fenprothrin were applied (Table 4.6). Aqueous sprays were applied using a Raven Pro 94.5 L boom sprayer fitted with TeeJet turbo nozzles at 30 psi (0.21 MPa) pulled by a tractor at slow speed (gear 1). Finished spray was applied at 52.9 mL/m².

For a 2 lbs ai/A application rate, 103 mL of malathion was mixed with 6.5 gallons of water in the tank to deliver 56.6 gal/A. In Study 3, an indicator dye for visual determination of the actual surface area of the glove contacting treated turf. Becker Underwood® Spray Tracer Purple (1.5 oz/gal) was added to the tank mix however, no dye was visible on the latex gloves.

Another dye study was performed (without pesticide) with 7.5 oz/gal of indicator dye in 6.5 gallons of water. Cotton gloves, instead of latex, were used. See 4.3.8 for additional details.

In Study 4, an adjuvant was added to the tank mix to observe the effect on transferable pesticide residue. The tank mix consisted of 105 mL of malathion mixed with 6.5 gallons of water plus 2 oz/gal of Activator 90®, a non-ionic surfactant penetrant anti-foaming agent.

See Table 4.6 for “Study Periods, Application Rates and Tank Mix Measurements.”

4.3.6. Tank Mix Analysis

A tank mix with an application rate of 2 lbs/A malathion and fenpropathrin was prepared and the active ingredients analyzed to confirm source strength. Three 1000 ml samples were collected in Nalgene bottles directly from the tank spout. Samples were extracted by liquid:liquid extraction as follows: (1) 1 ml of tank mix was added with 99 ml of water in a separatory funnel (2) 70 ml of ethyl acetate was added to the aqueous solution, hand shaken and extracted (process was repeated 3 times to yield a total of 210 ml ethyl acetate) (3) total extract of 210 ml ethyl acetate was transferred to a round bottom flask and reduced to dryness using a Büchi rotary evaporator (4) sample was re-suspended in 50 ml ethyl acetate. Analysis of tank mix for malathion was evaluated using GC/MS. Aliquots of 1 µl of sample were injected into a HP 6890 Series GC/MS in split-less mode equipped with a 30 m x 0.25 mm x 0.25 µm DB1701 column (Agilent Technologies, Inc.) for analysis. The detection and quantification limits were 0.05 and 0.17 µg/ml, respectively. Malathion ions monitored were 173, 125 and 127.

GC/MS Settings:

Injector temp: 220°C
Carrier gas flow rate: 1.0 ml/min
Initial temp: 50 °C, hold 1 min

Ramp 1: 20°C/min to 180°C
Ramp 2: 10°C/min to 190°C
Ramp 3: 3°C/min to 240°C
Ramp 4: 10°C/min to 280°C, hold for 2 min
Solvent delay: 5 min: Total Run Time: 31.17 min

4.3.7. Spray Deposition

Deposition samples were used to determine the actual amount of malathion applied to the turf. Prior to application on Day 0, six cotton cloth coupons, cloth dosimeters folded several times to give a surface area of approximately 100 cm² lined with 100 cm² aluminum foil, were each anchored to the ground with a sharp wooden skewer at equally spaced locations on each turf bay (Figure 4.2). Cotton cloth coupons were collected immediately after application. The aluminum foil lining was discarded after sampling when it was determined that no breakthrough of spray had occurred. The cotton cloths were placed in quart-sized Ziploc® bags and immediately transferred back to the PCEP laboratory for extraction and analysis. See 4.3.7 “Recovery Studies” for methods of extraction and analysis.

4.3.8. Actual glove surface area contacting treated turf using the BCTU

To determine the actual surface area of gloved mannequin hands contacting treated turf, indicator dye Becker Underwood® Spray Tracer Purple was added to the tank mix in Study 3. Immediately after the application, a BCTU run on a “test” lane using rubber latex gloves and cotton gloves revealed no visible dye on either material.

The amount of indicator dye was increased from 1.5 oz/gal to 7.5 oz/gal in a second dye study without the use of any pesticides in the tank mix. Latex gloves did not stain well with Spray Tracer Purple, therefore, cotton gloves were used for surface area

measurements. In the dye study, runs 1, 2, 3 and 4 were performed to observe if contacted surface area remained consistent during multiple runs. After each run, the cotton gloves were carefully placed on aluminum foil, carefully wrapped to avoid cross contamination, labeled and transported back to the PCEP laboratory. At laboratory, the aluminum foil was opened on a flat counter-top and the samples were air dried. Once thoroughly dry, the cotton gloves were placed on cardboard with labels and photographed. Later, any purple stained areas on the cotton gloves were cut and placed in appropriately labeled Ziploc® bags. Using a leaf area meter (LI-3000A, LI-COR Biosciences, Lincoln, NE) the surface area of the cotton glove pieces was determined.

4.3.9. Extraction of Malathion From Latex Gloves, Polyethylene Bags and Cotton Cloths

4.3.9.1. *Latex Gloves*

A total of 9 pairs of clean rubber latex gloves (Rite Aid® Multi-Purpose Sanitary Latex Medical Powder Free Gloves) were spiked with liquid formulations of malathion in ethyl acetate. Spikes included three low, medium and high sample fortifications relative to levels measured during this research. Blank samples included a clean pair of rubber latex gloves. Each pair of rubber latex gloves were spiked within properly labeled quart sized Ziploc® bags. The Ziploc® bags were left open for 2-3 h to dry. Samples were stored in a freezer for 24 h prior to being extracted. Each pair of gloves were cut into small pieces and then extracted with 150 mL of ethyl acetate in the sample bag shaken at high frequency on an Eberbach shaker. The total extract was transferred to a round bottom flask and volume reduced to ~3-5 mL on a Büchi rotary evaporator. Remaining volume was air-dried using light air flow. Sample was re-

suspended in 1-5 mL ethyl acetate. Aliquots of 1 μ L of sample were injected into a HP 5890 Series II GC-FPD in split-less mode equipped with a 30 m x 0.25 mm HP-5MS column (Agilent Technologies, Inc.) for analysis. The limit of detection and limit of quantification were 0.611 and 2.04 μ g/mL, respectively. Method settings were saved as “TLOFPD”.

GC/FPD Settings:

Injector temp: 230°C
Detector temp: 250°C
Initial temp: 50 °C, hold 1 min
Ramp 1: 20 °C/min to 260 °C, hold for 15 mins
Total Run Time: 26.50 min

To ensure that any remaining residual ethyl acetate in the Ziploc® bags would not affect the results of the study, the pairs of gloves from the first recovery study were extracted a second time using the same extraction procedure. Weights of the bag, gloves and solvent were recorded.

4.3.9.2. Polyethylene Bags

Recoveries of malathion were also performed on the quart-sized freezer Ziploc® bags to ensure that pesticide residues were not being absorbed by the polyethylene-linear low density (LLDPE) bags. This was accomplished by spiking 9 quart-sized freezer Ziploc® bags with the same liquid formulation levels as in the initial glove recovery study. Similarly, extraction and recovery of malathion from the bags was measured using the same extraction procedure performed to extract the rubber latex gloves (4.3.9.1).

4.3.9.3. 100% White Cotton Cloths

The recovery of pesticide residues from cotton cloths was also evaluated. Cotton cloth dosimeters (1500 cm²), used to measure TTRs and spray deposition, were spiked

with low, medium and high levels of liquid formulations of malathion. After the cloths were allowed to dry (~30 min to 1 h), they were placed in labeled quart-sized freezer Ziploc® bags and stored in a freezer at -20°C for 24 to 36 h. A blank cotton cloth was included.

The cotton cloths were extracted with a 300 mL ethyl acetate in a Soxhlet apparatus. The apparatus was refluxed for 6 h. The total extract was transferred to a round bottom flask and volume reduced to ~3-5 mL on a Büchi rotary evaporator. Remaining volume was air-dried using light air flow. Sample was re-suspended in 1-5 mL ethyl acetate. Aliquots of 1 µL of sample were injected into a HP 5890 Series II GC-FPD in split-less mode equipped with a 30 m x 0.25 mm HP-5MS column (Agilent Technologies, Inc.) for analysis. Weights of the bags, 1500 cm² cotton cloths and solvent were recorded.

4.3.10. Data Analysis

Sample concentrations were calculated in Microsoft Excel using linear regression of a 5 point standard curve (linearity range: 1-50ppm GC-FPD). Means and standard deviations of data were calculated using Microsoft Excel. Statistical comparisons were calculated using Statistical Analysis Software v.9.2 (SAS®) and Minitab 16 Statistical Software.

4.4. Results and Discussion

4.4.1. Malathion Recovery Studies

4.4.4.1. Recovery of Malathion From Rubber Latex Gloves

Recovery of malathion from rubber latex gloves ranged from 104-141% after spiking with 5, 50 and 250 µg/ml malathion (Table 4.7: Recovery 2). A second glove rinse was performed to identify if any residual malathion remained following the usual extraction scheme. The second glove rinse recoveries ranged from 9-21% (Table 4.7: Recovery 3). The residual malathion resulted primarily from the 13 mL of solvent remaining in the Ziploc® bags. Residual solvent (13 mL) was determined gravimetrically and recoveries adjusted by the resulting 150 mL (nominal)/137 mL (measured) correction factor (Table 4.7).

4.4.1.2. Recovery of Malathion From Polyethylene Bags

Concerns regarding the possible absorption of pesticide residues by the polyethylene-linear low density (LLDPE) bags (Ziploc®) led to an extensive recovery study of malathion from the bags. After spiking bags with 5, 50 and 250 µg/ml of malathion, malathion recoveries ranged from 82.3% to 90.7% (Table 4.7: Recovery 1). There was no evidence that malathion adsorption interfered with use of the polyethylene bags during sample handling and extraction of the insecticide.

4.4.1.3. Recovery of Malathion From 100% White Cotton Cloths

The recovery of malathion from 100% white cotton cloths ranged from 119-154% after spiking with 5, 20 and 100 µg/ml malathion (Table 4.8: Recovery 1). A second extraction of the cotton cloths resulted in recoveries ranging from 1.6-88.7% (Table 4.8: Recovery 2). High recovery from the second extraction of the cotton cloths is the result of one sample, of the 3, from the 5 µg/ml fortification level registering 195% recovery. The other two samples fortified at 5 µg/ml were within the normal range (60-120%).

4.4.2. Spray Application and Deposition Analysis

Malathion was applied at a nominal rate of 2 lbs/A or 22.4 $\mu\text{g}/\text{cm}^2$ to turf (Table 4.9). Deposition coupons (100 cm^2 cotton cloths) revealed malathion was deposited on turf at rates of 9.7 $\mu\text{g}/\text{cm}^2$ and 7.9 $\mu\text{g}/\text{cm}^2$ in Studies 3 and 4 (Table 4.9). The spray deposition rates² ($\mu\text{g}/\text{cm}^2$) for Study 3 were 10.2 ± 1.7^a and $9.2 \pm 1.5^{a,c}$, and 7.0 ± 1.1^b and 8.7 ± 1.0^c for Study 4. There was no significant difference of spray deposition between Bays 1 and 2 in Study 3 and Bay 2 between studies 3 and 4 (p-values > 0.05). There was a significant difference between Bays in Study 4 (p-values < 0.05). Deposition rates of 9.7 $\mu\text{g}/\text{cm}^2$ and 7.9 $\mu\text{g}/\text{cm}^2$ implied that only 43% and 35% of malathion was applied to turf based on the nominal application rate of 22.4 $\mu\text{g}/\text{cm}^2$. However, analysis of tank mix showed that only 54% and 40% of malathion was found in the tank mix with the exception of one malathion recovery of 127%, which is likely due to an analytical error (see footnote Table 4.10). Based on analysis of tank mix and resulting depositions found on the cotton cloth coupons, the actual percent of spray mix deposited on turf was 92% and 75% in Studies 3 and 4 (Table 4.11).

4.4.3. Transferable Turf Residues (TTRs)

Average malathion Transferable Turf Residues (TTRs) measured using the CDFA roller ranged from 0.002-0.117 $\mu\text{g}/\text{cm}^2$ from all study periods (Table 4.12). Highest residues (TTRs) observed were on day 1 of each study period. Regardless of slight differences in tank mix measurements used for each study (Table 4.6), a pair-wise

² Spray deposition values with same letter superscripts indicates no significant differences between those values. Different letter superscripts indicates a significant difference between the values (^{a,b,c}).

statistical comparison using the General Linear Model (GLM) Procedure showed that there is no significant difference (p -values > 0.05) between TTRs from each study.

All studies (1,2,3,and 4) showed a time-dependent dissipation of TTRs (Table 4.12; Figures 4.3 to 4.6). In Study 1, TTRs dropped from $0.076 \mu\text{g}/\text{cm}^2$ to $0.015 \mu\text{g}/\text{cm}^2$ (Table 4.12; Figure 4.3) following 2 precipitation events (0.03 inches and 0.27 inches: Table 4.2). This situation was also observed during Study 3 (Figure 4.5) when TTRs rapidly decreased following rainfall on day 3 (0.14 inches of rain: Table 4.4). Studies 2 and 4 showed time-dependent reduction of TTR (Figures 4.4 and 4.6). In Study 2, a spike in TTR ($0.065 \mu\text{g}/\text{cm}^2$ to $0.096 \mu\text{g}/\text{cm}^2$: Table 4.12; Figure 4.4) on day 3 was likely the result of moisture from morning dew or high humidity (71% humidity; Table 4.3). Zweig et al. (1985) concluded that high humidity had a positive effect on pesticide transfer from foliage to cloth monitors confirming current observations. Additionally, Williams et al. (2002) determined that moisture increases chemical transferability from a nylon carpet. A similar observation was made among strawberry harvesters (Zhang, 2005).

The percent malathion residue recovered and transferred from treated turf to cotton cloth dosimeters (1500 cm^2) using the CDFA roller ranged from 0.02% to 1.21% from all studies (Table 4.13) based on deposition values from cotton cloth coupons and TTRs in $\mu\text{g}/\text{cm}^2$ (Table 4.9). The percent transferred residue in these turf studies was lower than the findings from Ross et al. (1991) where percent transferred residue ranged from 1 to 3 percent from indoor floor surface pesticide residues after use of an indoor fogger (Ross et al., 1991). The half-life of malathion using cotton cloth dosimeters over the course of 7 to 13 d study periods was approximately 2.2 days (Table 4.14).

4.4.4. Actual glove surface area contacting treated turf using the BCTU, “Dye Study”

The nominal surface area of the rubber latex glove dosimeters contacting treated turf was assumed to be 420 cm² to represent the surface area of the average adult human hand (Table 1.1; EPA, 2007). Harvester glove residues likely are unevenly distributed over the entire surface area of the hands of harvesters. Using cotton gloves to absorb dye permits the pattern of glove contact with turf to be visualized. Actual surface area of the cotton gloved mannequin hands contacting turf ranged from 44.8-108.3 cm² when the dyed area of the gloves was averaged (Table 4.15). Highest contact surface area was recorded at 132.9 cm² in run 4 for hand B. Hand contact surface area increased with the number of runs (time). Visual observations of the purple dye on the cotton gloves showed that the contact area was primarily isolated to the fingertips (Figures 4.7 to 4.10).

As the number of runs increased, contact surface area became saturated with purple indicator dye which may have dispersed the dye over a larger surface area on the cotton glove than actually contacted turf. Though the highest contact surface area recorded was 132.9 cm², it was not used to represent latex glove area due to the following considerations: (1) recorded contact surface area using indicator dye changed as the number of runs increased (contact surface area should remain constant) (2) the dye likely diffused as the cotton became saturated (3) there was variability from each hand therefore a contact surface area constant for all hands cannot be used (4) indicator dye sprayed on turf may not be equally distributed on leaf blades (i.e. beading up and falling off of dye on leaf blade) and may not transfer to mannequin hands consistently (5) measurements of dye on cotton gloves was visual and not measured quantitatively. As a result of these

limitations in determination of actual contact surface area, the default 420 cm² hand surface area was used to represent surface area of the hand. Nonetheless, variability seen by the dye between mannequin hands and the increase in dye transfer with the number of runs indicates that residue transfer is dependent on the extent of turf contact.

4.4.5. Pesticide Glove Residues (PGRs) and Target Application Rate

The initial application rate of malathion was 1 lb ai/A. The amount of residue accumulated on gloves (18 µg/glove to 64 µg/glove) was too low to evaluate residue transfer over several days (Table 4.16). Therefore, to establish a longer study period, the application rate was increased to 2 lbs ai/A for later studies (Table 4.6).

4.4.6. Variability Between Contact-Transfer To Mannequin Hands

By visual observation of the BCTU, hand B seemed to have more surface contact than hands A and C (Tables 4.16 to 4.20; Figures 4.11 to 4.14). This is likely a result of uneven distribution of the two 2 lb weights added to the BCTU to ensure consistent contact of the mannequin hands to turf. A paired T-test showed that PGRs from hand B were significantly different than those from hands A and C from all studies (p-value < 0.05). This indicates that residue accumulation on gloves is contact-dependent. This finding also supports the conclusion that each mannequin hand on the BCTU acted as an independent sampling unit (Hand A, B, C) and should be treated as such.

4.4.7. Residue Accumulation on Gloves During Runs Over Treated Turf

Pesticide glove residues (PGRs) evaluated up to 13 d post application for malathion (2 lbs/A), showed increased accumulation of residue as runs increased (Study 2; Figure 4.15). The differences run-to-run indicated that residue accumulation on gloves

was time-dependent. A paired T-test showed that there was no significant difference between PGRs ($\mu\text{g/glove}$) from each run ($p\text{-values} > 0.05$; particularly study 2) indicating that the rate of accumulation as runs increased was not significantly different. This resulted from the relatively consistent rate of residue accumulation from each run (Tables 4.21 to 4.24).

A decline in residue accumulation beyond 3 runs (Figure 4.15) was observed in Study 2. This was likely due to saturation and redistribution of residue back to treated foliage after extensive contact. This observation is consistent with findings by Li (2009) where physical removal of pesticide residues using an Automatic Surface Wipe device and different stroke cycles on a treated leaf surface showed that the first contact was the most important when residues were at their highest. Subsequent sampling produced smaller amounts of residue. Similarly, highest accumulated residues are obtained from run 3 using the BCTU (i.e. Study 2, Day 1, Run 3: $156 \mu\text{g/glove}$ - $398 \mu\text{g/glove}$; Table 4.18). A decline in residue accumulation on gloves is seen on run 4 (i.e. Study 2, Day 1, Run 3: $129 \mu\text{g/glove}$ - $266 \mu\text{g/glove}$; Table 4.18) only when residues are at their highest.

In Study 4, use of a sticker spreader adjuvant, Activator 90®, greatly reduced the amount of residue accumulation on gloves during all runs (Table 4.20). PGRs therefore did not reach their point of highest residue in turn allowing further accumulation of residue by run 4 (Figure 4.15).

4.4.8. Dissipation of Turf Residue

4.4.8.1. Time

Malathion PGRs showed biphasic exponential turf residue decay (Figures 4.11 to 4.14). Glove residues represent dissipation of surface residue on turf. The dissipation of the surface residue on turf monitored using rubber latex gloves showed a time-dependent reduction of malathion residue over a 13 d study period (PGRs: 398 µg/glove–day 1 to 0.1 µg/glove–day 13; Tables 4.16 to 4.20; Figures 4.11 to 4.14).

4.4.8.2. Precipitation

Rain on day 4 of Study 1 and day 3 of Study 3 (Tables 4.17 and 4.19) abruptly reduced PGR. Study 1 day 3 PGRs ranged from 20 µg/glove to 248 µg/glove but after the rain the PGRs were only 5 µg/glove (Tables 4.17; Figure 4.11). This finding is consistent with classification of OPs as highly susceptible to washoff by rain (Wise, 2010).

In the turf studies, after a precipitation event, pesticide residue availability and transfer to gloves would be dependent on the rainfastness of the pesticide product (in this case malathion). A pesticide product is considered “rainfast” when rainfall or irrigation no longer reduces the performance of the product and can no longer be washed off by rain (DiFonzo, <http://fieldcrop.msu.edu/sites/fieldcrop/files/RainfallperiodsforInsecticides.pdf>). Herbicide labels commonly provide information on rainfastness since it is important for the product to be held on the leaf for a length of time to get adequate uptake of the active ingredient into the plant (DiFonzo, <http://fieldcrop.msu.edu/sites/fieldcrop/files/RainfallperiodsforInsecticides.pdf>). Insecticide labels often do not give a rainfast period since insecticide products kill by contact at the time of treatment. In studies utilizing a rainfall simulation chamber conducted at Michigan State University, a number of insecticide classes were compared under the basis of their rainfastness and it

was determined that organophosphate insecticides have the highest susceptibility to wash-off from precipitation (Table 4.25). Therefore, it is expected that residue availability for transfer from treated foliage to gloves would greatly be affected by the occurrence of rainfall in these studies utilizing turf and the BCTU. Since these studies were conducted during the winter season, precipitation events occurred during study periods.

4.4.8.3. Spray Adjuvant: Activator 90®

Residue dissipation was also affected by the addition of an adjuvant in the tank mix in Study 4 (Figure 4.14: Table 4.20). PGRs were lower in Study 4 (2 µg/glove to 178 µg/glove: Table 4.20) compared to PGRs in Study 2 (0.1 µg/glove to 398 µg/glove: Table 4.18). Low PGRs levels seen from Study 4 may have been the result of the adjuvants affect on the formulation of the pesticide as a sticker spreader therefore, residues were not readily transferrable to gloves during sampling. This possibility warrants further study. It is important to note that TTR levels from Study 4 showed expected dissipation of turf residue (section 4.4.3) whereas PGR levels from the same study period were affected by use of an adjuvant.

The transfer of pesticide residues to gloves from treated turf may be affected by the use of spray adjuvants dependent. Adjuvants are substances that modify biological activity and application characteristics of an agrochemical by changing the physical and chemical properties of the spray mixture (Green, 2000). Adjuvants can be mixed into a tank solution or found within a pesticide formulation. U.S. regulatory agencies pay less attention to the regulation of adjuvants than active ingredients, however, in California, it

is a requirement that adjuvants are registered and regulated (Tu and Randall, 2003).

Adjuvants are classified by function and chemistry however most products have multi-functional purposes thereby making them difficult to categorize (Tables 4.26 and 4.27).

In this study utilizing turf and the BCTU model systems, the adjuvant used was Activator 90® (Loveland Products®, Inc., Greeley, CO.; Appendices 8 and 9) a non-ionic surfactant penetrant, anti-foaming agent with quick wetting and spreader sticking properties (Tables 4.26 and 4.27). As a spreader sticker, it is expected that the transfer of pesticide residues from treated turf to gloves is reduced with the use of Activator 90® in the spray mix.

A pair-wise statistical comparison using the General Linear Model (GLM) Procedure (SAS® v.9.1) showed that there is no significant difference (p -values > 0.05) in malathion residue accumulation on gloves (PGRs) between studies specific to hands and runs (Study 1: 3-298 $\mu\text{g/glove}$, Study 2: 0.1-398 $\mu\text{g/glove}$, Study 3: 2-308 $\mu\text{g/glove}$, Study 4: 3-179 $\mu\text{g/glove}$). This indicates that the results are consistent and reproducible using the BCTU. The pattern of residue accumulation in study 4 (Figure 4.14) differed from that in studies 1,2, and 3 (Figures 4.11 to 4.13), however, the overall range of residue accumulation was not statistically different among the 4 studies. Overall, the half-life of malathion using glove dosimeters over the course of 7 to 13 d study periods was approximately 1.4 days (Table 4.14).

4.4.9. Percent Malathion Residue Recovered and Transferred

Pesticide Glove Residues (PGRs) expressed in ug/cm^2 seen in Tables 4.28 to 4.31 show the amount of residues accumulated (0.0003-0.95 ug/cm^2) on the average adult

human hand (420 cm²; Table 1.1; EPA, 2007). The percent of malathion residue transferred and recovered from turf to gloves (Tables 4.32 to 4.35) was determined by comparing mean deposition in µg/cm² (total residue deposited to turf measured by cotton cloth coupons; Table 4.9) and the amount of residue accumulated on gloves in µg/cm² (assuming a 420 cm² glove area; Tables 4.28 to 4.31). Studies 1, 2 and 3 used a 9.7 µg/cm² deposition value measured from Study 3 which was representative of a 2 lb/A application rate. Study 4 used a 7.9 µg/cm² deposition rate measured from day 0 of the same study (see section 4.4.2 and Table 4.9). The highest percent transferred and recovered residue from turf to gloves was from Day 1 of each Study (up to 10% transferred; Tables 4.32 to 4.35). The percent recovered residue was time-dependent since the amount of available residue dissipated over time (Figure 4.16). Less than 1% of the residue was recovered and transferred to gloves by day 5 from each Study (Tables 4.32 to 4.35).

4.4.10 Comparison of Transferable Surface Residues by the CDFA Roller and BCTU and Determination of a Transfer Factor

The CDFA roller utilizes a cotton cloth to collect transferable turf residue (TTRs) from treated turf (1500 cm²). The BCTU employs rubber latex gloves to collect transferable residue while being passed over treated turf. Both methods operate by contact transfer. The highest amount of residue accumulated on gloves (µg/glove) by the BCTU is 3 orders of magnitude greater than the highest amount of transferable residue accumulated on cotton cloths by the CDFA roller under the same conditions (Tables 4.12 and 4.16 to 4.20). The percent of recovered and transferred residue from treated turf to

cotton cloth dosimeters utilizing the CDFA roller ranged from 0.02% to 1.21% whereas the percent recovered and transferred residue from turf to gloves utilizing the BCTU ranged from 0.003% to 10% (both based upon spray deposition; Tables 4.32 to 4.35). When PGR was plotted as a function of TTR the regression demonstrated the strong correlation of these 2 measurements of transferability (availability) of surface residues (Figures 4.17 to 4.20).

The slope (PGRs ($\mu\text{g/glove}$)/TTRs ($\mu\text{g}/\text{cm}^2$)) represents an empirical transfer factor in cm^2/glove from each study (Table 4.36). An average transfer factor of 1548 cm^2/glove was determined from studies 1, 2 and 3. Study 4 included malathion plus an adjuvant (Activator 90[®]). The effect of the transfer of residue from treated turf to gloves resulted in lower PGR levels whereas TTR levels remained consistent study-to-study (section 4.4.7).

4.5. Conclusions

Experimental studies utilizing the BCTU and turf support the use of gloves as a direct dosimeter of harvester exposure. The accumulation of pesticide residues on gloves was dependent on the extent of contact to treated foliage determined by hand variability (i.e. hand B more heavily weighted therefore accumulated more residue) and increased residue over runs (time). The percent malathion residue recovered and transferred from treated turf to a gloved mannequin hand (assuming 420 cm^2 surface area) ranged from <1% to 10% based on deposition measurements. Latex glove dosimeters also accumulated multiple pesticide residues as determined by concurrent applications of malathion and fenpropathrin (data not shown) to turf and in field studies reported in

Chapter 3. Gloves accumulated 2.6 times more malathion residue than fenproprathrin in studies utilizing turf (overall, 0.5-146 $\mu\text{g/glove}$ –fenproprathrin and 0.14–398 $\mu\text{g/glove}$ –malathion). This observation is consistent with recent field observations (Santa Maria, CA; 2010) where gloves accumulated 2.1 times more malathion residue than fenproprathrin on harvester gloves under the same field conditions. PGRs dissipated by biphasic exponential decay over time and first-order PGR half-lives were approximately 1.4 d for malathion and 4.6 d for fenproprathrin. Both insecticides were highly susceptible to wash-off by rain and the amount of transferable residue was also affected by the addition of an adjuvant in the tank mix.

TTRs ($\mu\text{g}/\text{cm}^2$), determined using the CDFA roller and cotton cloth dosimeters, also dissipated by biphasic exponential decay over time for both malathion and fenproprathrin. First order TTR half-lives were approximately 2.2 d for malathion and 3 d for fenproprathrin. When the accumulation of transferable surface residues were compared using the two contact transfer methods (BCTU and CDFA roller), it was determined that residues accumulated on cotton cloths (TTRs: 0.002-0.117 $\mu\text{g}/\text{cm}^2$) were less than the amounts accumulated on gloves (PGRs: 0.14-398 $\mu\text{g/glove}$ or 0.0003-0.95 ug/cm^2 assuming a 420 cm^2 surface area). Additionally, PGRs accumulated up to 10% of transferrable residue whereas cotton cloth dosimeters accumulated only 1.2%. In the presence of moisture, latex gloves did not show any changes in residue accumulation at any time during these studies. However, cotton cloth dosimeters showed a spike in residue accumulation on day 3 of Study 2 (Figure 4.4) when morning dew was present (Table 4.3). This is likely the result of the high absorbent material of cotton cloths (Zweig

et al. 1985; Zhang 2005). When plotting PGRs ($\mu\text{g}/\text{glove}$) as a function of TTRs ($\mu\text{g}/\text{cm}^2$), high regression correlation coefficients were observed ($R^2 = 0.5\text{--}1.0$) indicating that the residue transfer was consistent over time by both contact transfer methods. Additionally, an average empirical transfer factor of $1548 \text{ cm}^2/\text{glove}$ was derived from the resulting slope from studies 1, 2 and 3. This empirical transfer factor approximates residue transfer estimates in cm^2/glove by contact transfer methods (using the BCTU and CDFA roller). Additional studies are required to clarify this transfer factor.

Studies by Ross et al. (1991) utilizing the CDFA roller on indoor floor surfaces after use of a fogger showed a 1 to 3 percent transfer of residues whereas current measures transferred up to 1.2 percent. Differences in results are likely the cause of different sampling media and environmental conditions. After a 1 lb/A application of chlorpyrifos to turf and a measured deposition of $12 \pm 4 \mu\text{g}/\text{cm}^2$ using cotton lined aluminum foil dosimeters, Bernard et al. (2001) approximated $0.085 \pm 0.024 \mu\text{g}/\text{cm}^2$ was transferred to cotton cloth dosimeters using the CDFA roller. Current studies where malathion was applied at a 2 lb/A application rate and measured a $9.7 \pm 1.6 \mu\text{g}/\text{cm}^2$ deposition accumulated $0.081 \pm 0.06 \mu\text{g}/\text{cm}^2$ (day 1, Study 3) from treated turf to cotton cloths using the CDFA roller. Current findings were consistent with those determined by Bernard et al. (2001) indicating that the CDFA roller is an excellent, reproducible measure of transferrable surface residues.

Preliminary field studies by Li et al. (2011) where harvesters wore light rubber latex gloves for a 2 to 2.5 h period shown an accumulation of malathion residues ranging from 481 to 1670 $\mu\text{g}/\text{pair}$ ($n=10$) at the 3-day preharvest interval (PHI) when residues

were highest (Li et al., 2011). Malathion residues accumulated on gloves during 1 to 4 continuous contact runs with treated turf ranged from 0.14-398 µg/glove. Malathion field PGRs (Santa Maria, CA; 2011) accumulated 19.2-times more residue than malathion PGRs from controlled turf studies. In both cases, malathion glove residue levels declined biphasically over time. First-order malathion half-lives were 2.7 d from harvester gloves during the initial 18 d study period (Li et al., 2011) and 1.4 d by surrogate monitoring utilizing turf during a 13 d study period. Differences in residue accumulation and dissipation over time were likely the result of the extent of contact to treated foliage (2.5 h contact vs. surrogate monitoring up to 4 runs), treated matrix (turf vs. strawberry leaves) and sampling conditions.

Glove sampling using the BCTU on treated turf was intended to draw a relationship between surrogate monitoring and actual field observations. While some similarities were identified (i.e. biphasic dissipation of residue over time—up to 13 d), differences were likely the result of limitations to using the BCTU. A primary limitation to using the BCTU for surrogate dermal monitoring was not being able to sample for extended periods of time. Thus limiting the amount of contact the gloves can come to treated foliage. Relatively large amounts of treated turf are required for single experiments and variability is high due to environmental factors that are difficult to assess and control (i.e. condition of the turf, weather, moisture etc.).

4.6. References

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Table 4.1: Pilot Study Sampling Times and Environmental Conditions

Study Period: November 15, 2010 – November 20, 2010

Application: malathion (1 lb/A)

Test Day	Activity	Sampling Time	Temperature during sampling (°F)	Precipitation (in.)	Dew Point (°F)	Relative humidity (%)	Presence of moisture (Y/N) ^a	Weather conditions	Temperature (High Low)°F
0	Sprayed	0800 *	57	0	36	45	N	Clear	79 49
1	sampled	1000	67	0	41	39	N	Clear	77 48
2				0					81 47
3	sampled	1100	75	0	35	23	N	Partly Cloudy	81 48
4				0.03					61 56
5				0.31					59 53
6				0.18					59 46
7	sampled	1000	54	0	40	59	N	Partly Cloudy	61 41

*No samples were taken. Observations were recorded for time of application.

^aThe presence of moisture on turf may be a result of precipitation, morning dew, or unintentional irrigation. Any amount of moisture, whether saturated or light dew, are recorded as “Y”.

Table 4.2: Study 1 Sampling Times and Environmental Conditions

Study Period: December 2, 2010 – December 9, 2010

Application: malathion (2 lbs/A)

Test Day	Activity	Sampling Time	Temp. during sampling (°F)	Precip. (in.)	Dew Point (°F)	Relative humidity (%)	Presence of moisture (Y/N) ^a	Weather conditions	Temp. (High Low) °F
0	sprayed	0900 *	58	0	27	31	N	Clear	79 44
1	sampled	1100	67	0	29	24	N	Partly Cloudy	74 44
2				0					67 45
3	sampled	1100	51	0.03	49	92	Y	Light rain	69 44
4				0.27					67 48
5	sampled	1100	72	0	37	28	N	Clear	79 44
6				0					76 44
7	sampled	1100	64	0	38	38	N	Clear	72 44

*No samples were taken. Observations were recorded for time of application.

^aThe presence of moisture on turf may be a result of precipitation, morning dew, or unintentional irrigation. Any amount of moisture, whether saturated or light dew, are recorded as “Y”.

Table 4.3: Study 2 Sampling Times and Environmental Conditions

Study Period: January 6, 2011 – January 19, 2011

Application: malathion (2 lbs/A) and fenpropathrin (2 lbs/A)

Test Day	Activity	Sampling Time	Temperature during sampling (°F)	Precipitation (in.)	Dew Point (°F)	Relative humidity (%)	Presence of moisture (Y/N) ^a	Weather conditions	Temperature (High Low)°F
0	sprayed	0900 *	62 *	0	20	20	N	Clear	71 47
1	sampled	1100	56	0	37	49	N	Clear	59 45
2				0					55 46
3	sampled	1100	52	0	43	71	Y	Mostly Cloudy	58 49
4				0					63 42
5	sampled	1100	61	0	17	18	N	Mostly Cloudy	65 46
6				0					73 45
7	sampled	1100	72	0	30	21	N	Scattered Clouds	76 48
8				0					78 53
9	sampled	1100	78	0	30	17	N	Clear	84 59
10	Irrigated			0					80 48
11	Irrigated/ sampled	1100	79	0	50	36	Y	Clear	85 57
12	Irrigated			0					85 51
13	Irrigated/ sampled	1100	66	0	48	52	Y	Scattered Clouds	72 49

*No samples were taken. Observations were recorded for time of application.

^aThe presence of moisture on turf may be a result of precipitation, morning dew, or unintentional irrigation. Any amount of moisture, whether saturated or light dew, are recorded as “Y”.

Table 4.4: Study 3 Sampling Times and Environmental Conditions

Study Period: January 27, 2011 – February 9, 2011

Application: malathion (2 lbs/A), fenpropathrin (2 lbs/A) and Becker Underwood® Spray Tracer Purple

Test Day	Activity	Sampling Time	Temperature during sampling (°F)	Precipitation (in.)	Dew Point (°F)	Relative humidity (%)	Presence of moisture (Y/N) ^a	Weather conditions	Temperature (High Low)°F
0	sprayed/deposition	1000	68	0	27	21	N	Clear	77 43
1	sampled	1100	68	0	25	20	N	Clear	75 41
2				0					70 40
3	sampled	1100	55	0.14	43	64	Y	Light rain	56 49
4				0					63 43
5	sampled	1100	55	0	45	69	Y	Mostly cloudy	63 41
6				0					59 43
7	sampled	1100	58	0	8	14	N	Clear	64 34
8				0					69 34
9	sampled	1100	62	0	46	56	N	Clear	72 40
10				0					80 45
11	sampled	1100	76	0	37	24	N	Clear	77 48
12				0					66 44
13	sampled	1100	63	0	16	16	N	Clear	68 53

*No samples were taken. Observations were recorded for time of application.

^aThe presence of moisture on turf may be a result of precipitation, morning dew, or unintentional irrigation. Any amount of moisture, whether saturated or light dew, are recorded as “Y”.

Table 4.5: Study 4 Sampling Times and Environmental Conditions

Study Period: March 28, 2011 – April 10, 2011

Application: malathion (2 lbs/A), fenpropathrin (2 lbs/A) and Activator 90®

Test Day	Activity	Time of Activity	Temperature during activity (°F)	Daily Precipitation (in.)	Dew Point (°F)	Relative humidity (%)	Presence of moisture (Y/N) ^a	Weather conditions	Temperature (High Low)°F
0	sprayed/ deposition	1100	61	0	48	62	Y	Partly cloudy	67 50
1	sampled	1000	60	0	51	72	N	Haze	78 47
2				0					88 52
3	sampled	1000	81	0	48	31	N	Clear	97 56
4				0					92 59
5	sampled	0900	60	0	55	83	Y	Haze	77 56
6				0					69 56
7	sampled	1000	74	0	34	23	N	Clear	86 48
8				0					79 51
9	sampled	1000	60	0	51	72	N	Overcast	69 52
10				0					69 56
11	sampled	1000	49	0.04	33	54	N	Scattered clouds	57 44
12				0.02					60 37
13	sampled	1100	57	0	38	49	N	Clear	71 41

*No samples were taken. Observations were recorded for time of application.

^aThe presence of moisture on turf may be a result of precipitation, morning dew, or unintentional irrigation. Any amount of moisture, whether saturated or light dew, are recorded as “Y”

Table 4.6: Study Periods, Application Rates and Tank Mix Measurements

Study	Pesticide Applied	Application Rate (lb ai/A)	Tank Mix		
			Pesticide (mL)	Water (gal)	Additives (oz/gal)
Pilot	malathion	1	54	9	N/A
1	malathion	2	103	6.5	N/A
2	malathion	2	103	6.5	N/A
	fenpropathrin	2	103		
3	malathion	2	103	6.5	1.5 ^a
	fenpropathrin	2	103		
“dye”	N/A	N/A	N/A	6.5	7.5 ^a
4	malathion	2	105	6.5	2.0 ^b
	fenpropathrin	2	105		

^a Becker Underwood® Spray Tracer Purple indicator dye

^b Activator 90®, a non-ionic surfactant penetrant anti-foaming agent

Table 4.7: Method Validation and Recovery of Malathion**Recovery 1 - Bag recovery studies**

Pesticide ^a	Linearity range ^b (µg/ml)	R ²	LOD ^c (µg/ml)	LOQ ^d (ug/ml)	Fortification level ^e (µg/ml)	Recovery ± SD ^f (%)	RSD ^g (%)
malathion	1-100	0.9999	0.611	2.04	5	86.4 ± 3.7	4
					50	82.3 ± 4.5	5
					250	90.7 ± 3.7	4

Recovery 2 - Glove recovery studies

Pesticide ^a	Linearity range ^b (µg/ml)	R ²	LOD ^c (µg/ml)	LOQ ^d (ug/ml)	Fortification level ^e (µg/ml)	Recovery ± SD ^f (%)	RSD ^g (%)
malathion	1-100	0.9999	0.611	2.04	5	104.4 ± 9.6	9
					50	141.3 ± 4.5	3
					250	126.1 ± 12.3	10

Recovery 3- Glove second rinse recovery studies

Pesticide ^a	Linearity range ^b (µg/ml)	R ²	LOD ^c (µg/ml)	LOQ ^d (ug/ml)	Fortification level ^e (µg/ml)	Recovery ± SD ^f (%)	RSD ^g (%)
malathion	1-100	0.9999	0.611	2.04	5	21.1 ± 1.5	7
					50	10.3 ± 1.2	11
					250	9.1 ± 1.2	13

^a Pesticide applied on a pair of rubber latex gloves in one-quart polyethylene Ziploc bag.

^b Standard curve range on GC-ECD and GC-FPD.

^c Limit of Detection of the GC-FPD for malathion.

^d Limit of Quantification of the GC-FPD for malathion.

^e Fortification levels used as liquid spikes.

^f Residual solvent(13 mL) was determined gravimetrically and recoveries adjusted with 150 mL (nominal)/137 mL (measured) correction factor =1.09.

^g Percent Relative Standard Deviation is the absolute value of the coefficient of variation

Table 4.8: Recovery of Malathion From 1500 cm² Cotton Cloth Dosimeters

Recovery 1 – Cotton cloth recovery

Pesticide ^a	Linearity range ^b (µg/ml)	R ²	LOD ^c (µg/ml)	LOQ ^d (ug/ml)	Fortification level ^e (µg/ml)	Recovery ± SD ^f (%)	RSD ^g (%)
malathion	1-50	0.9934	0.611	2.04	5	123.7 ± 20.8	17
					20	153.9 ± 11.8	8
					100	119.4 ± 5.0	4

Recovery 2 – Cotton cloth recovery second rinse

Pesticide ^a	Linearity range ^b (µg/ml)	R ²	LOD ^c (µg/ml)	LOQ ^d (ug/ml)	Fortification level ^e (µg/ml)	Recovery ± SD ^f (%)	RSD ^g (%)
malathion	1-50	0.9934	0.611	2.04	5	88.7 ± 92.4*	104
					20	9.4 ± 2.1	23
					100	1.56 ± 0.1	3

*One sample, out of three, had a high recovery (195%). Samples 1 and 2 recoveries were 31.7% and 39.1% respectively. Therefore average overall recovery was 88.7%.

^a Pesticide applied on a 1500 cm² cotton cloth.

^b Standard curve range on GC-FPD.

^c Limit of Detection of the GC-FPD for malathion.

^d Limit of Quantification of the GC-FPD for malathion.

^e Fortification levels used as liquid spikes.

^f Average adjusted recovery with 300 mL (nominal)/244 mL (measured) correction factor.

^g Percent Relative Standard Deviation is the absolute value of the coefficient of variation as a percent.

Table 4.9: Summary of Malathion Spray Deposition Results

Sample coupon ^a	$\mu\text{g}/\text{cm}^2$			
	Study 3		Study 4	
	Bay 1	Bay 2	Bay 1	Bay 2
1	8.6	8.9	7.1	7.5
2	10.7	11.5	5.8	9.5
3	9.4	8.5	6.1	8.6
4	8.6	9.4	6.6	8.4
5	13.0	9.8	7.8	8.2
6	10.7	6.9	8.6	10.2
Mean	10.2	9.2	7.0	8.7
S.D.	1.7	1.5	1.1	1.0
C.V.	16.4	16.7	15.6	11.3
Combined Mean	9.7		7.9	

Nominal ^b	22.4			
Actual (%) ^c	45	41	31	39
Mean (%) ^d	43		35	

^a Measured spray deposition was sampled with 100 cm² cotton cloth coupons at 6 defined locations on each Bay (Figure 4.2).

^b Application rate for studies 3 and 4 was 2 lbs/A or 22.4 $\mu\text{g}/\text{cm}^2$ (nominal).

^c Actual percent of application spray deposited is based on nominal calculation ((mean/nominal) x100).

^d Mean percent is the average of the actual (%) deposited from the two Bays

Table 4.10: Tank Mix Analysis and Verification on GC

Analysis ^a (n=3)	Instrument	Linearity range ^b (µg/ml)	R ²	LOD ^c (µg/ml)	LOQ ^d (ug/ml)	Recovery ± SD (%)	RSD ^e (%)
1	GC/MS	0.5-50	0.9886	0.05	0.17	127 ± 36.8 ^f	29
2	GC/MS	0.5-50	0.9974	0.05	0.17	54 ± 9.0	17
3	GC/FPD	1-50	0.9992	0.61	2.04	40 ± 10.8	27

^a A total of 3 samples were taken from the same tank mix at the same time. Tank mix was analyzed on GC/MS and GC/FPD.

^b Standard curve range on GC/MS and GC/FPD.

^c Limit of Detection of the GC/MS and GC/FPD for malathion.

^d Limit of Quantification of the GC/MS and GC/FPD for malathion.

^e Percent Relative Standard Deviation is the absolute value of the coefficient of variation.

^f Initial analysis of tank mix resulted in 127% (95%, 119%, 167%) recovered malathion. High recovery led to additional analysis of the same tank mix samples (analysis 2 and 3). Since analyses 2 and 3 showed similar results, their corresponding recoveries were used for the determination of the amount of malathion present in the tank mix.

Table 4.11: Actual Percent of Spray Mix Deposited (Based on Analysis of Tank Mix)

	Study 3		Study 4	
	Bay 1	Bay 2	Bay 1	Bay 2
Nominal^a	22.4			
Actual % (coupons)^b	45	41	31	39
Mean % (coupons)^c	43		35	

Mean Tank Mix (%)^d	47			
% Sprayed^e	92		75	

^a Application rate for studies 3 and 4 was 2 lbs/A or 22.4 µg/cm² (nominal).

^b Actual percent of application spray deposited is based on nominal calculation ((mean/nominal) x100) (Table 4.9).

^c Mean % was derived from actual percent of spray deposition applied to Bays 1 and 2.

^d Mean percent malathion in tank mix determined by tank mix analysis 2 and 3 (Table 4.10).

^e Percent of malathion sprayed shows that 92% and 75% of all malathion found in the tank mix was sprayed on turf.

Table 4.12: Summary of Transferrable Turf Residues (TTRs)

Average Transferrable Turf Residues (TTRs) in $\mu\text{g}/\text{cm}^2$					
Day	Study				
	Pilot $n^a = 3$	1 $n = 3$	2 $n = 4$	3 $n = 4$	4 $n = 4$
1	0.022 ± 0.003	0.117 ± 0.03	0.065 ± 0.01	0.081 ± 0.06	0.053 ± 0.02
3	0.013 ± 0.0003	$0.076 \pm 0.03^*$	0.096 ± 0.02	$0.046 \pm 0.01^*$	0.043 ± 0.005
5	N/S*	0.015 ± 0.0001	0.024 ± 0.005	0.008 ± 0.001	0.040 ± 0.01
7	N/D	0.015 ± 0.0001	0.018 ± 0.005	0.005 ± 0.0004	0.019 ± 0.0001
9	N/S	N/S	0.010 ± 0.002	0.002 ± 0.00	0.0097 ± 0.001
11	N/S	N/S	$0.006 \pm 0.001^\dagger$	0.002 ± 0.00	$0.0034 \pm 0.00^*$
13	N/S	N/S	$0.002 \pm 0.00^\dagger$	0.002 ± 0.00	0.0033 ± 0.00

Average Transferrable Turf Residues (TTRs) measured using the CDFA and cotton cloth dosimeters (1500 cm^2) from each study.

^a number of samples taken each day during study.

“N/S” indicates no sample.

“N/D” indicates non-detectable

*A precipitation event occurred on or after sampling day.

[†]Unexpected irrigation event.

Table 4.13: Percent Recovered and Transferred Turf Residue (TTR) From Treated Turf to Cotton Cloth Dosimeters by CDFA Roller

% Recovered and Transferred ^a				
(ug/cm² TTRs) ^b/(ug/cm² deposited) ^c = %				
Day	Study			
	1	2	3	4
1	1.21	0.68	0.84	0.67
3	0.79*	0.99	0.48*	0.55
5	0.15	0.25	0.08	0.51
7	0.15	0.18	0.06	0.24
9	N/S	0.11	0.02	0.12
11	N/S	0.06†	0.02	0.04*
13	N/S	0.02†	0.02	0.04

^a Percent recovered and transferred malathion residues from turf to cotton cloth dosimeters when comparing mean deposition value from cotton coupons (total residue deposited to turf) to the amount of residue found on cotton cloths (TTRs).

^b Transferrable Turf Residues (TTRs) measured from 1500 cm² cotton cloth dosimeters.

^c Mean deposition of 9.66 µg/cm² from cotton cloth coupons (100 cm²) was used for Studies 1, 2 and 3 (representative of a 2 lbs/A application rate). Mean deposition of 7.87 µg/cm² was used for Study 4.

*A precipitation event occurred on or after sampling day

†Unanticipated irrigation occurred on or after sampling day.

Table 4.14: Malathion Half-lives From Pesticide Glove Residues (PGRs) and Transferable Turf Residues (TTRs) for Each Study Period

Study	Days ^a	n ^b	PGRs		DFRs	
			t _{1/2} (Days) ^c	R ^d	t _{1/2} (Days)	R
# 1	7	3	0.96	-0.95	1.79	-0.93
# 2	13	4	1.50	-0.92	2.32	-0.96
# 3	13	4	1.79	-0.96	2.05	-0.93
# 4	13	4	1.20	-0.77	2.60	-0.96
Average (Days)			1.4		2.2	

^a Total days in the study.

^b Number of runs in each study.

^c First-order half-life were calculated as $t_{1/2} = \ln(2)/k$. Half-life was determined from daily average residues from each Study (Tables 4.19 to 4.22).

^d Average Pearson's correlation (R) from plotting malathion residue and time in days.

Table 4.15: Actual Glove Surface Area (cm²) Contacting Turf Using Gloved Mannequin Hands

Type of glove and Run Number	Hand (cm ²)			Average	% of nominal ^a
	A	B	C		
Cotton Gloves - 1 Run Test	26.8	43.5	50.5	40.3	9.6
Latex Gloves - 1 Run Test	50.8	72.9	29.9	51.2	12.2
Cotton Gloves - Run 1	65.5	40.1	28.8	44.8	10.7
Cotton Gloves - Run 2	70.7	64.5	51.7	62.3	14.8
Cotton Gloves - Run 3	69.3	77.9	74.1	73.8	17.6
Cotton Gloves - Run 4	105.0	132.9	86.9	108.3	25.8

^a Percent of total surface area of rubber latex glove dosimeter. The total surface area of the glove is assumed to be 420 cm² in correlation with the exposed skin surface area from one hand of the average adult (EPA Dermal Exposure Assessment, 2007).

Table 4.16: Pilot Study Pesticide Glove Residues (PGRs)

Study Period: November 15, 2010 – November 20, 2010

Application: malathion (1 lb/A)

Pesticide Glove Residues (PGR) ($\mu\text{g}/\text{glove}$)					
Day	Hand	Run			Average
		1	2	3	
1	A	18.8	23.6	37.2	32.8
	B	20.0	32.3	64.2	
	C	16.8	34.5	47.6	
3	A	18.3	21.7	18.3	18.9
	B	18.2	18.5	19.0	
	C	18.1	18.8	19.3	
5*	A	N/S	N/S	N/S	N/S
	B	N/S	N/S	N/S	
	C	N/S	N/S	N/S	
7	A	N/D	N/D	N/D	N/D
	B	N/D	N/D	N/D	
	C	N/D	N/D	N/D	

Pesticide Glove Residues (PGRs) were sampled using the BCTU on treated turf. A single latex glove was sampled from each mannequin hand labeled (A, B, C) to identify their position within the chassis of the modified lawn mower. Glove samples were collected after each Run. N/S indicates no sample taken. N/D indicates non-detectable. *A precipitation event occurred on or after sampling day.

Table 4.17: Study 1 Pesticide Glove Residues (PGRs)

Study Period: December 2, 2010 – December 9, 2010

Application: malathion (2 lbs/A)

Pesticide Glove Residues (PGR) (ug/glove)					
Day	Hand	Run			Average
		1	2	3	
1	A	35.0	123.3	216.8	170.7
	B	98.3	210.4	297.7	
	C	126.2	209.7	218.5	
3*	A	20.3	66.0	118.6	106.3
	B	50.4	107.8	247.9	
	C	57.8	124.5	163.2	
5	A	4.4	4.4	4.7	4.7
	B	4.5	4.8	5.0	
	C	4.7	5.2	5.1	
7	A	3.0	3.1	3.1	3.2
	B	3.0	3.3	3.2	
	C	3.2	3.2	3.4	

Pesticide Glove Residues (PGRs) were sampled using the BCTU on treated turf. A single latex glove was sampled from each mannequin hand labeled (A, B, C) to identify their position within the chassis of the modified lawn mower. Glove samples were collected after each Run. *A precipitation event occurred on or after sampling day.

Table 4.18: Study 2 Pesticide Glove Residues (PGRs)

Study Period: January 6, 2011 – January 19, 2011

Application: malathion (2 lbs/A) and fenpropathrin (2 lbs/A)

Pesticide Glove Residues (PGR) (ug/glove)						
Day	Hand	Run				Average
		1	2	3	4	
1	A	39.0	66.6	174.5	201.5	151.3
	B	97.8	154.8	397.5	266.8	
	C	64.5	67.6	156.1	129.0	
3	A	24.2	52.0	76.6	60.8	61.7
	B	41.2	76.1	155.4	108.6	
	C	23.4	24.2	43.6	54.7	
5	A	13.2	15.3	30.4	23.7	23.3
	B	15.4	17.2	53.8	38.5	
	C	10.2	11.3	27.7	37.3	
7	A	18.1	20.0	31.2	24.4	22.5
	B	18.5	20.2	34.4	28.2	
	C	16.3	17.7	19.0	21.7	
9	A	4.6	18.0	32.6	22.7	23.1
	B	17.6	21.6	42.1	31.7	
	C	14.2	16.3	24.4	20.3	
11†	A	0.7	0.6	1.3	0.9	0.9
	B	0.5	0.6	1.9	1.7	
	C	0.4	0.6	0.6	0.5	
13†	A	0.2	0.6	0.9	0.5	0.4
	B	0.2	0.6	0.7	0.4	
	C	0.1	0.3	0.2	0.5	

Pesticide Glove Residues (PGRs) were sampled using the BCTU on treated turf. A single latex glove was sampled from each mannequin hand labeled (A, B, C) to identify their position within the chassis of the modified lawn mower. Glove samples were collected after each Run. †Unanticipated irrigation occurred on or after sampling day.

Table 4.19: Study 3 Pesticide Glove Residues (PGRs)

Study Period: January 27, 2011 – February 9, 2011

Application: malathion (2 lbs/A), fenpropathrin (2 lbs/A) and Becker Underwood® Spray Tracer Purple

Pesticide Glove Residues (PGR) (ug/glove)						
Day	Hand	Run				Average
		1	2	3	4	
1	A	72.5	139.4	162.6	205.4	170.3
	B	104.0	210.6	308.2	269.1	
	C	46.8	127.9	200.9	195.9	
3*	A	26.1	43.7	69.8	152.3	67.0
	B	26.3	49.4	105.1	138.8	
	C	14.8	43.3	53.0	81.8	
5	A	17.4	18.7	20.3	21.3	19.5
	B	17.5	20.3	22.2	25.1	
	C	16.4	18.2	18.4	17.7	
7	A	9.5	9.7	11.3	11.4	10.1
	B	9.4	9.9	10.5	11.3	
	C	9.1	9.5	10.0	10.1	
9	A	2.2	2.2	2.3	2.5	2.3
	B	2.2	2.3	2.5	2.2	
	C	2.1	2.2	2.2	2.3	
11	A	1.6	1.6	1.7	1.7	1.6
	B	1.6	1.6	1.7	1.8	
	C	1.6	1.6	1.6	1.6	
13	A	2.2	2.1	2.3	2.2	2.1
	B	2.1	2.3	2.2	2.1	
	C	2.1	2.1	2.0	2.1	

Pesticide Glove Residues (PGRs) were sampled using the BCTU on treated turf. A single latex glove was sampled from each mannequin hand labeled (A, B, C) to identify their position within the chassis of the modified lawn mower. Glove samples were collected after each Run. *A precipitation event occurred on or after sampling day.

Table 4.20: Study 4 Pesticide Glove Residues (PGRs)

Study Period: March 28, 2011 – April 10, 2011

Application: malathion (2 lbs/A), fenpropathrin (2 lbs/A) and Activator 90®

Pesticide Glove Residues (PGR) (ug/glove)						
Day	Hand	Run				Average
		1	2	3	4	
1	A	28.6	45.9	56.5	73.2	73.9
	B	38.5	62.1	120.7	150.4	
	C	11.8	42.0	78.3	178.9	
3	A	2.1	2.8	3.7	4.0	3.7
	B	2.9	3.7	5.1	6.7	
	C	1.5	2.3	3.4	6.4	
5	A	4.3	5.5	5.9	5.0	5.7
	B	6.1	5.7	6.8	7.9	
	C	3.4	4.3	5.2	7.9	
7	A	N/D	N/D	N/D	N/D	N/D
	B	N/D	N/D	N/D	N/D	
	C	N/D	N/D	N/D	N/D	
9	A	N/D	N/D	N/D	N/D	N/D
	B	N/D	N/D	N/D	N/D	
	C	N/D	N/D	N/D	N/D	
11*	A	N/D	N/D	N/D	N/D	N/D
	B	N/D	N/D	N/D	N/D	
	C	N/D	N/D	N/D	N/D	
13	A	N/D	N/D	N/D	N/D	N/D
	B	N/D	N/D	N/D	N/D	
	C	N/D	N/D	N/D	N/D	

Pesticide Glove Residues (PGRs) were sampled using the BCTU on treated turf. A single latex glove was sampled from each mannequin hand labeled (A, B, C) to identify their position within the chassis of the modified lawn mower. Glove samples were collected after each Run. N/D indicates non-detectable. *A precipitation event occurred on or after sampling day.

Table 4.21: Study 1 Normalized Pesticide Glove Residues (PGRs)

Study Period: December 2, 2010 – December 9, 2010

Application: malathion (2 lbs/A)

Normalized Pesticide Glove Residues (PGRs) (ug/cm ² /run) ^a				
Day	Hand	Run		
		1	2	3
1	A	0.08	0.15	0.17
	B	0.23	0.25	0.24
	C	0.30	0.25	0.17
3*	A	0.05	0.08	0.09
	B	0.12	0.13	0.20
	C	0.14	0.15	0.13
5	A	0.01	0.01	0.004
	B	0.01	0.01	0.004
	C	0.01	0.01	0.004
7	A	0.01	0.004	0.002
	B	0.01	0.004	0.003
	C	0.01	0.004	0.003

^a Pesticide Glove Residues (PGRs) were normalized for glove area (assumed: 420 cm²) and runs calculated as ug/cm²/run. Normalized PGRs show accumulation rate on gloves per run. *A precipitation event occurred on or after sampling day.

Table 4.22: Study 2 Normalized Pesticide Glove Residues (PGRs)

Study Period: January 6, 2011 – January 19, 2011

Application: malathion (2 lbs/A) and fenpropathrin (2 lbs/A)

Normalized Pesticide Glove Residues (PGRs) (ug/cm ² /run) ^a					
Day	Hand	Run			
		1	2	3	4
1	A	0.09	0.08	0.14	0.12
	B	0.23	0.18	0.32	0.16
	C	0.15	0.08	0.12	0.08
3	A	0.06	0.06	0.06	0.04
	B	0.10	0.09	0.12	0.07
	C	0.06	0.03	0.04	0.03
5	A	0.03	0.02	0.02	0.01
	B	0.04	0.02	0.04	0.02
	C	0.02	0.01	0.02	0.02
7	A	0.04	0.02	0.03	0.02
	B	0.04	0.02	0.03	0.02
	C	0.04	0.02	0.02	0.01
9	A	0.01	0.02	0.03	0.01
	B	0.04	0.03	0.03	0.02
	C	0.03	0.02	0.02	0.01
11 [†]	A	0.002	0.001	0.001	0.001
	B	0.001	0.001	0.002	0.001
	C	0.001	0.001	0.001	0.0003
13 [†]	A	0.0004	0.001	0.001	0.0003
	B	0.001	0.001	0.001	0.0002
	C	0.0003	0.0004	0.0002	0.0003

^a Pesticide Glove Residues (PGRs) were normalized for glove area (assumed: 420 cm²) and runs calculated as ug/cm²/run. Normalized PGRs show accumulation rate on gloves per run. [†]Unanticipated irrigation occurred on or after sampling day.

Table 4.23: Study 3 Normalized Pesticide Glove Residues (PGRs)

Study Period: January 27, 2011 – February 9, 2011

Application: malathion (2 lbs/A), fenpropathrin (2 lbs/A) and Becker Underwood® Spray Tracer Purple

Normalized Pesticide Glove Residues (PGRs) (ug/cm ² /run) ^a					
Day	Hand	Run			
		1	2	3	4
1	A	0.17	0.17	0.13	0.12
	B	0.25	0.25	0.25	0.16
	C	0.11	0.15	0.16	0.12
3*	A	0.06	0.05	0.06	0.09
	B	0.06	0.06	0.08	0.08
	C	0.04	0.05	0.04	0.05
5	A	0.04	0.02	0.02	0.01
	B	0.04	0.02	0.02	0.02
	C	0.04	0.02	0.02	0.01
7	A	0.02	0.01	0.01	0.01
	B	0.02	0.01	0.01	0.01
	C	0.02	0.01	0.01	0.01
9	A	0.005	0.003	0.002	0.001
	B	0.005	0.003	0.002	0.001
	C	0.005	0.003	0.002	0.001
11	A	0.004	0.002	0.001	0.001
	B	0.004	0.002	0.001	0.001
	C	0.004	0.002	0.001	0.001
13	A	0.005	0.003	0.002	0.001
	B	0.005	0.003	0.002	0.001
	C	0.005	0.002	0.002	0.001

^a Pesticide Glove Residues (PGRs) were normalized for glove area (assumed: 420 cm²) and runs calculated as ug/cm²/run. Normalized PGRs show accumulation rate on gloves per run. *A precipitation event occurred on or after sampling day.

Table 4.24: Study 4 Normalized Pesticide Glove Residues (PGRs)

Study Period: March 28, 2011 – April 10, 2011

Application: malathion (2 lbs/A), fenpropathrin (2 lbs/A) and Activator 90®

Normalized Pesticide Glove Residues (PGRs) (ug/cm²/run) ^a					
Day	Hand	Run			
		1	2	3	4
1	A	0.07	0.06	0.05	0.04
	B	0.09	0.07	0.10	0.09
	C	0.03	0.05	0.06	0.11
3	A	0.01	0.003	0.003	0.002
	B	0.01	0.004	0.004	0.004
	C	0.004	0.003	0.003	0.004
5	A	0.01	0.01	0.01	0.003
	B	0.02	0.01	0.01	0.01
	C	0.01	0.01	0.004	0.01
7	A	N/D	N/D	N/D	N/D
	B	N/D	N/D	N/D	N/D
	C	N/D	N/D	N/D	N/D
9	A	N/D	N/D	N/D	N/D
	B	N/D	N/D	N/D	N/D
	C	N/D	N/D	N/D	N/D
11*	A	N/D	N/D	N/D	N/D
	B	N/D	N/D	N/D	N/D
	C	N/D	N/D	N/D	N/D
13	A	N/D	N/D	N/D	N/D
	B	N/D	N/D	N/D	N/D
	C	N/D	N/D	N/D	N/D

^a Pesticide Glove Residues (PGRs) were normalized for glove area (assumed: 420 cm²) and runs calculated as ug/cm²/run. Normalized PGRs show accumulation rate on gloves per run. *A precipitation event occurred on or after sampling day.

Table 4.25: Rainfastness Rating Chart: General Characteristics for Insecticide Chemical Classes

Insecticide Class	Rainfastness ≤ 0.5 inch		Rainfastness ≤ 1.0 inch		Rainfastness ≤ 2.0 inch	
	Fruit	Leaves	Fruit	Leaves	Fruit	Leaves
Organophosphates	L	M	L	M	L	L
Pyrethroids	M	M	L	M	L	L
Carbamates	M	M	L	M	L	L
IGRs	M	H				
Neonicotinoids	M,S	H,S	L,S	L,S	L,S	L,S
Spinosyns	H	H	H	M	M	L
Diamides	H	H	H	M	M	L
Avermectins	M,S	H,S	L,S	M,S	L	L

* H – highly rainfast ($\leq 30\%$ residue wash-off), M – moderately rainfast ($\leq 50\%$ residue wash-off), L – low rainfast ($\leq 70\%$ residue wash-off), S-systemic residues remain within plant tissue (Wise, 2010).

Table 4.26: Some of the Terminology Used for Adjuvants on Pesticide and Adjuvant Labels

Activator	Acidifying Agent	Additive
Antifoam/Defoam	Antifreeze	Attractant
Buffering Agent	Chelating Agent	Cleaner
Colorant / Dye	Compatibility Agent	Coupler
Crop Oil Concentrate	Deposition Agent	Detergent
Dispersant	Drift Control Agent	Emulsifier
Evaporation Reducer	Extender	Fertiliser
Foam Marker	Formulant	Humectant
Inert	Modified Seed Oil	Neutraliser
Penetrator	Petroleum Oil	Preservative
Rainfast Agent	Retention Aid	Solubilizer
Surfactant	Spreader Sticker	Synergist
Thickener	Translocation Aid	UV Protectant
Vegetable Oil	Water Conditioner	Wetting Agent

Reference: (Green, 2000)

Table 4.27: Activator 90® classifications and descriptions

Activator 90® classifications	description
activator	enhances pesticide activity
non-ionic	has no ionic charge, is hydrophilic and generally biodegradable
surfactant	enhances the emulsifying, dispersing, spreading, sticking or wetting properties of the pesticide tank mix
penetrant	helps dissolve waxy cuticles ^b
anti-foaming	reduces or suppresses the formation of foam in spray tanks
quick-wetting	lowers surface tension in the spray droplet and allows the pesticide formulation to form a large thin layer on target plant
spreader sticker	reduces losses of formulation from target plants (losses due to evaporation of droplets from target surface, droplets beading-up and falling off)

Compilation of Activator 90® (Appendices 8 and 9) classifications as described by product label (Loveland Products®, Inc., Greeley, CO.) with descriptions from Tu & Randall, 2003. ^b description from Tonkin, 2002.

Table 4.28: Study 1 Pesticide Glove Residues (PGRs) Expressed in $\mu\text{g}/\text{cm}^2$

Study Period: December 2, 2010 – December 9, 2010

Application: malathion (2 lbs/A)

Pesticide Glove Residues (PGRs) in $\mu\text{g}/\text{cm}^2$				
Day	Hand	Run		
		1	2	3
1	A	0.08	0.29	0.52
	B	0.23	0.50	0.71
	C	0.30	0.50	0.52
3*	A	0.05	0.16	0.28
	B	0.12	0.26	0.59
	C	0.14	0.30	0.39
5	A	0.01	0.01	0.01
	B	0.01	0.01	0.01
	C	0.01	0.01	0.01
7	A	0.01	0.01	0.01
	B	0.01	0.01	0.01
	C	0.01	0.01	0.01

Pesticide Glove Residues (PGRs) expressed in $\mu\text{g}/\text{cm}^2$ show the amount of residue accumulated on the average adult human hand (average adult human hand: 420 cm^2 ; EPA, 2007). *A precipitation event occurred on or after sampling day.

Table 4.29: Study 2 Pesticide Glove Residues (PGRs) Expressed in $\mu\text{g}/\text{cm}^2$

Study Period: January 6, 2011 – January 19, 2011

Application: malathion (2 lbs/A) and fenpropathrin (2 lbs/A)

Pesticide Glove Residues (PGRs) in $\mu\text{g}/\text{cm}^2$					
Day	Hand	Run			
		1	2	3	4
1	A	0.09	0.16	0.42	0.48
	B	0.23	0.37	0.95	0.64
	C	0.15	0.16	0.37	0.31
3	A	0.06	0.12	0.18	0.15
	B	0.10	0.18	0.37	0.26
	C	0.06	0.06	0.10	0.13
5	A	0.03	0.04	0.07	0.06
	B	0.04	0.04	0.13	0.09
	C	0.02	0.03	0.07	0.09
7	A	0.04	0.05	0.07	0.06
	B	0.04	0.05	0.08	0.07
	C	0.04	0.04	0.05	0.05
9	A	0.01	0.04	0.08	0.05
	B	0.04	0.05	0.10	0.08
	C	0.03	0.04	0.06	0.05
11†	A	0.002	0.001	0.003	0.002
	B	0.001	0.002	0.005	0.004
	C	0.001	0.001	0.002	0.001
13†	A	0.0004	0.002	0.002	0.001
	B	0.001	0.001	0.002	0.001
	C	0.0003	0.001	0.001	0.001

Pesticide Glove Residues (PGRs) expressed in $\mu\text{g}/\text{cm}^2$ show the amount of residue accumulated on the average adult human hand (average adult human hand: 420 cm^2 ; EPA, 2007). †Unanticipated irrigation occurred on or after sampling day.

Table 4.30: Study 3 Pesticide Glove Residues (PGRs) Expressed in $\mu\text{g}/\text{cm}^2$

Study Period: January 27, 2011 – February 9, 2011

Application: malathion (2 lbs/A), fenpropathrin (2 lbs/A) and Becker Underwood® Spray Tracer Purple

Pesticide Glove Residues (PGRs) in $\mu\text{g}/\text{cm}^2$					
Day	Hand	Run			
		1	2	3	4
1	A	0.17	0.33	0.39	0.49
	B	0.25	0.50	0.73	0.64
	C	0.11	0.30	0.48	0.47
3*	A	0.06	0.10	0.17	0.36
	B	0.06	0.12	0.25	0.33
	C	0.04	0.10	0.13	0.20
5	A	0.04	0.04	0.05	0.05
	B	0.04	0.05	0.05	0.06
	C	0.04	0.04	0.04	0.04
7	A	0.02	0.02	0.02	0.03
	B	0.02	0.02	0.03	0.03
	C	0.02	0.02	0.02	0.02
9	A	0.01	0.01	0.01	0.01
	B	0.01	0.01	0.01	0.01
	C	0.01	0.01	0.01	0.01
11	A	0.004	0.004	0.004	0.004
	B	0.004	0.004	0.004	0.004
	C	0.004	0.004	0.004	0.004
13	A	0.01	0.01	0.01	0.01
	B	0.01	0.01	0.01	0.01
	C	0.01	0.01	0.01	0.01

Pesticide Glove Residues (PGRs) expressed in $\mu\text{g}/\text{cm}^2$ show the amount of residue accumulated on the average adult human hand (average adult human hand: 420 cm^2 ; EPA, 2007). *A precipitation event occurred on or after sampling day.

Table 4.31: Study 4 Pesticide Glove Residues (PGRs) Expressed in $\mu\text{g}/\text{cm}^2$

Study Period: March 28, 2011 – April 10, 2011

Application: malathion (2 lbs/A), fenpropathrin (2 lbs/A) and Activator 90®

Pesticide Glove Residues (PGRs) in $\mu\text{g}/\text{cm}^2$					
Day	Hand	Run			
		1	2	3	4
1	A	0.07	0.11	0.14	0.17
	B	0.09	0.15	0.29	0.36
	C	0.03	0.10	0.19	0.43
3	A	0.01	0.01	0.01	0.01
	B	0.01	0.01	0.01	0.02
	C	0.004	0.01	0.01	0.02
5	A	0.01	0.01	0.01	0.01
	B	0.02	0.01	0.02	0.02
	C	0.01	0.01	0.01	0.02
7	A	N/D	N/D	N/D	N/D
	B	N/D	N/D	N/D	N/D
	C	N/D	N/D	N/D	N/D
9	A	N/D	N/D	N/D	N/D
	B	N/D	N/D	N/D	N/D
	C	N/D	N/D	N/D	N/D
11*	A	N/D	N/D	N/D	N/D
	B	N/D	N/D	N/D	N/D
	C	N/D	N/D	N/D	N/D
13	A	N/D	N/D	N/D	N/D
	B	N/D	N/D	N/D	N/D
	C	N/D	N/D	N/D	N/D

Pesticide Glove Residues (PGRs) expressed in $\mu\text{g}/\text{cm}^2$ show the amount of residue accumulated on the average adult human hand (average adult human hand: 420 cm^2 ; EPA, 2007). *A precipitation event occurred on or after sampling day.

Table 4.32: Study 1 Percent Malathion Residue Recovered and Transferred From Treated Turf to Latex Gloves

Study Period: December 2, 2010 – December 9, 2010

Application: malathion (2 lbs/A)

% Recovered and Transferred ^a				
(ug/cm² PGRs) ^b/(9.66 ug/cm² deposited) ^c = %				
Day	Hand	Run		
		1	2	3
1	A	0.86	3.04	5.34
	B	2.42	5.19	7.34
	C	3.11	5.17	5.39
3*	A	0.50	1.63	2.92
	B	1.24	2.66	6.11
	C	1.43	3.07	4.02
5	A	0.11	0.11	0.12
	B	0.11	0.12	0.12
	C	0.12	0.13	0.13
7	A	0.07	0.08	0.08
	B	0.07	0.08	0.08
	C	0.08	0.08	0.09

^a Percent recovered and transferred malathion residues from turf to gloves when comparing mean deposition value from cotton cloth coupons (total residue deposited to turf) to the amount of residue found on gloves. ^b The total surface area of the glove is assumed to be 420 cm² to correspond with the exposed skin surface area from one hand of the average adult (EPA Dermal Exposure Assessment, 2007). ^c Mean value deposition of 9.66 µg/cm² from cotton cloth coupons (100 cm²) from Study #3 (representative of 2 lbs/A application rate). *A precipitation event occurred on or after sampling day

Table 4.33: Study 2 Percent Malathion Residue Recovered and Transferred From Treated Turf to Latex Gloves

Study Period: January 6, 2011 – January 19, 2011

Application: malathion (2 lbs/A) and fenpropathrin (2 lbs/A)

% Recovered and Transferred ^a					
(ug/cm² PGRs) ^b/(9.66 ug/cm² deposited) ^c = %					
Day	Hand	Run			
		1	2	3	4
1	A	0.96	1.64	4.30	4.97
	B	2.41	3.81	9.79	6.57
	C	1.59	1.67	3.85	3.18
3	A	0.60	1.28	1.89	1.50
	B	1.01	1.88	3.83	2.68
	C	0.58	0.60	1.08	1.35
5	A	0.32	0.38	0.75	0.58
	B	0.38	0.42	1.33	0.95
	C	0.25	0.28	0.68	0.92
7	A	0.45	0.49	0.77	0.60
	B	0.46	0.50	0.85	0.70
	C	0.40	0.44	0.47	0.54
9	A	0.11	0.44	0.80	0.56
	B	0.43	0.53	1.04	0.78
	C	0.35	0.40	0.60	0.50
11†	A	0.02	0.01	0.03	0.02
	B	0.01	0.02	0.05	0.04
	C	0.01	0.02	0.02	0.01
13†	A	0.004	0.02	0.02	0.01
	B	0.005	0.01	0.02	0.01
	C	0.003	0.01	0.01	0.01

^a Percent recovered and transferred malathion residues from turf to gloves when comparing mean deposition value from cotton cloth coupons (total residue deposited to turf) to the amount of residue found on gloves. ^b The total surface area of the glove is assumed to be 420 cm² corresponds to the exposed skin surface area from one hand of the average adult (EPA, 2007). ^c Mean value deposition of 9.66 µg/cm² from cotton cloth coupons (100 cm²) from Study #3 (representative of 2 lbs/A application rate).

†Unanticipated irrigation occurred on or after sampling day.

Table 4.34: Study 3 Percent Malathion Residue Recovered and Transferred From Treated Turf to Latex Gloves

Study Period: January 27, 2011 – February 9, 2011

Application: malathion (2 lbs/A), fenpropathrin (2 lbs/A) and Becker Underwood® Spray Tracer Purple

% Recovered and Transferred ^a					
(ug/cm² PGRs) ^b/(9.66 ug/cm² deposited) ^c = %					
Day	Hand	Run			
		1	2	3	4
1	A	1.79	3.44	4.01	5.06
	B	2.56	5.19	7.60	6.63
	C	1.15	3.15	4.95	4.83
3*	A	0.64	1.08	1.72	3.75
	B	0.65	1.22	2.59	3.42
	C	0.37	1.07	1.31	2.02
5	A	0.43	0.46	0.50	0.52
	B	0.43	0.50	0.55	0.62
	C	0.40	0.45	0.45	0.44
7	A	0.24	0.24	0.28	0.28
	B	0.23	0.24	0.26	0.28
	C	0.22	0.23	0.25	0.25
9	A	0.05	0.05	0.06	0.06
	B	0.05	0.06	0.06	0.05
	C	0.05	0.05	0.06	0.06
11	A	0.04	0.04	0.04	0.04
	B	0.04	0.04	0.04	0.04
	C	0.04	0.04	0.04	0.04
13	A	0.05	0.05	0.06	0.05
	B	0.05	0.06	0.06	0.05
	C	0.05	0.05	0.05	0.05

^a Percent recovered and transferred malathion residues from turf to gloves when comparing mean deposition value from cotton cloth coupons (total residue deposited to turf) to the amount of residue found on gloves. ^b The total surface area of the glove is assumed to be 420 cm² corresponds to the exposed skin surface area from one hand of the average adult (EPA, 2007). ^c Mean value deposition of 9.66 µg/cm² from cotton cloth coupons (100 cm²) was determined during this study.

*A precipitation event occurred on or after sampling day.

Table 4.35: Study 4 Percent Malathion Residue Recovered and Transferred From Treated Turf to Latex Gloves

Study Period: March 28, 2011 – April 10, 2011

Application: malathion (2 lbs/A), fenpropathrin (2 lbs/A) and Activator 90®

% Recovered and Transferred ^a					
(ug/cm² PGRs) ^b/(7.87 ug/cm² deposited) ^c = %					
Day	Hand	Run			
		1	2	3	4
1	A	0.87	1.39	1.71	2.22
	B	1.17	1.88	3.65	4.55
	C	0.36	1.27	2.37	5.41
3	A	0.06	0.08	0.11	0.12
	B	0.09	0.11	0.15	0.20
	C	0.05	0.07	0.10	0.19
5	A	0.13	0.17	0.18	0.15
	B	0.19	0.17	0.21	0.24
	C	0.10	0.13	0.16	0.24
7	A	N/D	N/D	N/D	N/D
	B	N/D	N/D	N/D	N/D
	C	N/D	N/D	N/D	N/D
9	A	N/D	N/D	N/D	N/D
	B	N/D	N/D	N/D	N/D
	C	N/D	N/D	N/D	N/D
11*	A	N/D	N/D	N/D	N/D
	B	N/D	N/D	N/D	N/D
	C	N/D	N/D	N/D	N/D
13	A	N/D	N/D	N/D	N/D
	B	N/D	N/D	N/D	N/D
	C	N/D	N/D	N/D	N/D

^a Percent recovered and transferred malathion residues from turf to gloves when comparing mean deposition value from cotton cloth coupons (total residue deposited to turf) to the amount of residue found on gloves. ^b The total surface area of the glove is assumed to be 420 cm² corresponds to the exposed skin surface area from one hand of the average adult (EPA Dermal Exposure Assessment, 2007). ^c Mean value deposition of 7.87 µg/cm² from cotton cloth coupons (100 cm²) was determined during this study. *A precipitation event occurred on or after sampling day.

Table 4.36: Transfer Factors in (cm²/glove)

Study	Transfer Factor ^a	Average	S.D.	% C.V.
1	1595	1548	457	30
2	1069			
3	1980			
4 ^b	5625	---	---	---

^a Transfer factors were derived from plotting Pesticide Glove Residues (PGRs in µg/glove) as a function of Transferable Turf Residues (TTRs in µg/cm²). The resulting slope yields the transfer factor in cm²/glove (Figures 4.11 to 4.14).

^b Study 4 included an adjuvant (Activator 90[®]) which affected the transfer of residue from treated turf to gloves, therefore, the Transfer Factor determined from Study 4 was not used to derive the overall average.

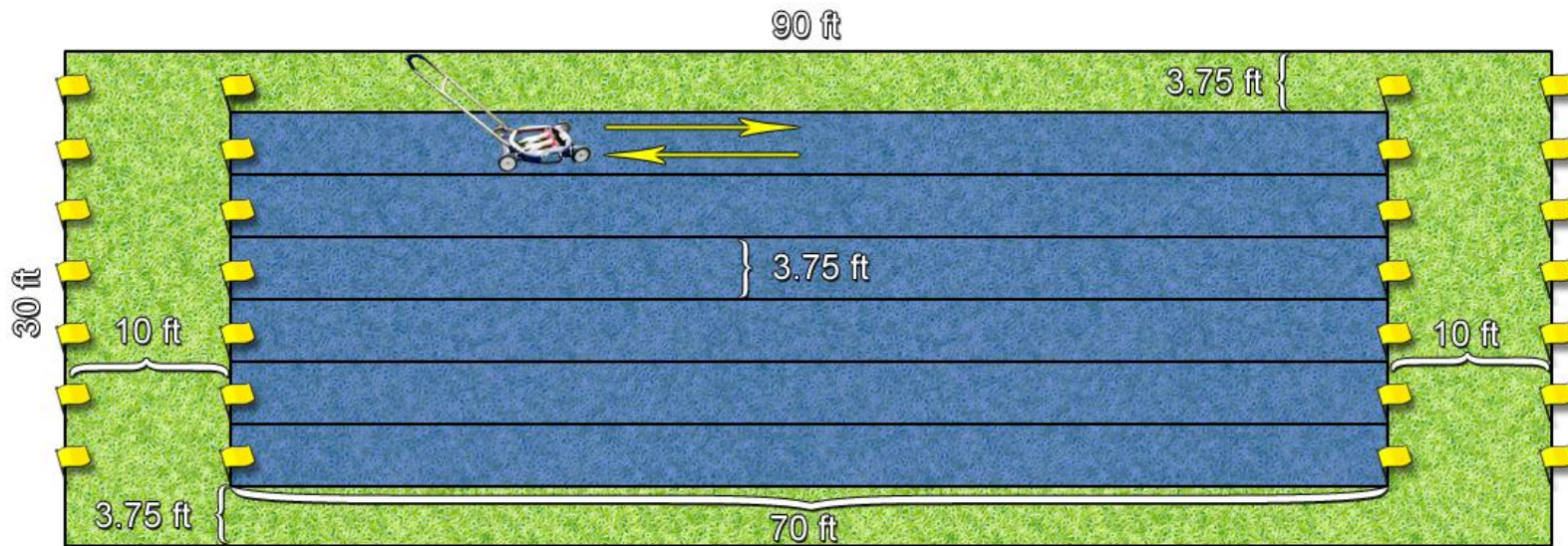


Figure 4.1: Measurements and Layout of Sampling Site for BCTU and CDFA Roller

Each turf bay was separated into 6 lanes approximately 3.75 ft wide for BCTU sampling runs. One run was one forward and one backward pass on the same lane. Two runs used 2 lanes, three runs used 3 lanes and four runs used 4 lanes. The 10 ft end-zones were used for sampling using the CDFA Roller.

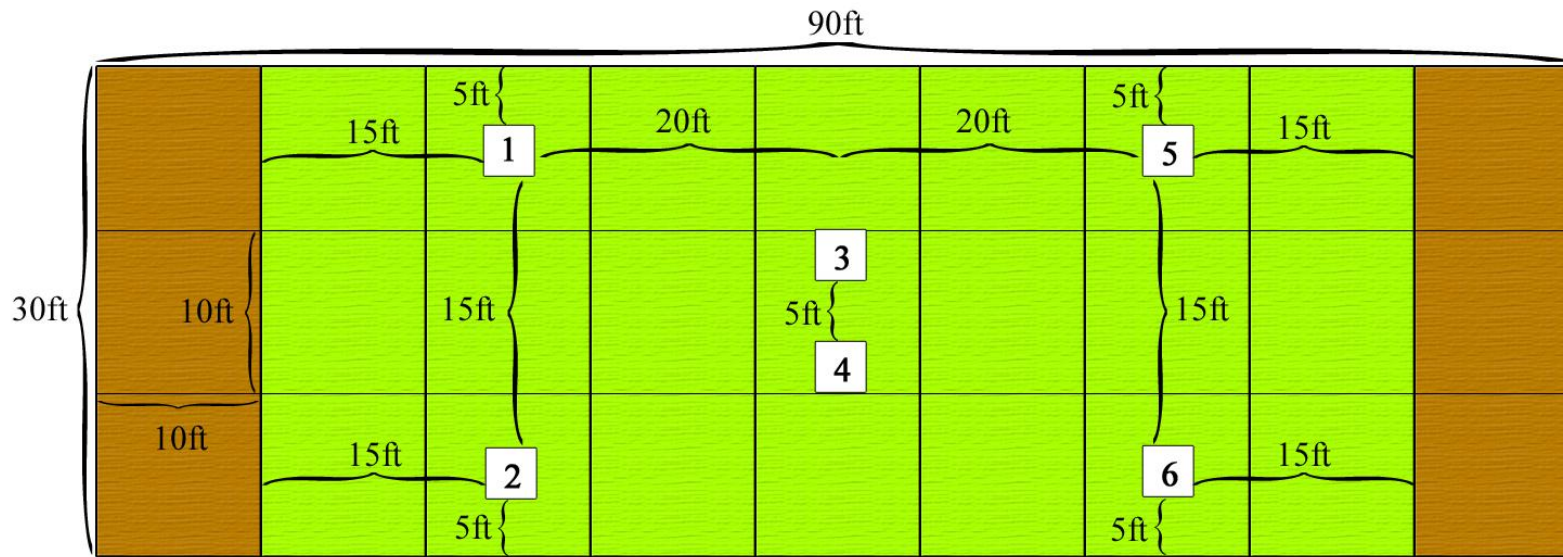


Figure 4.2: Measurements and Layout of Deposition Coupons On a Turf Bay

Six Coupons (layered cotton cloths lined with an aluminum foil backing) were anchored (using wooden skewers) to specific locations on each turf bay prior to pesticide application.

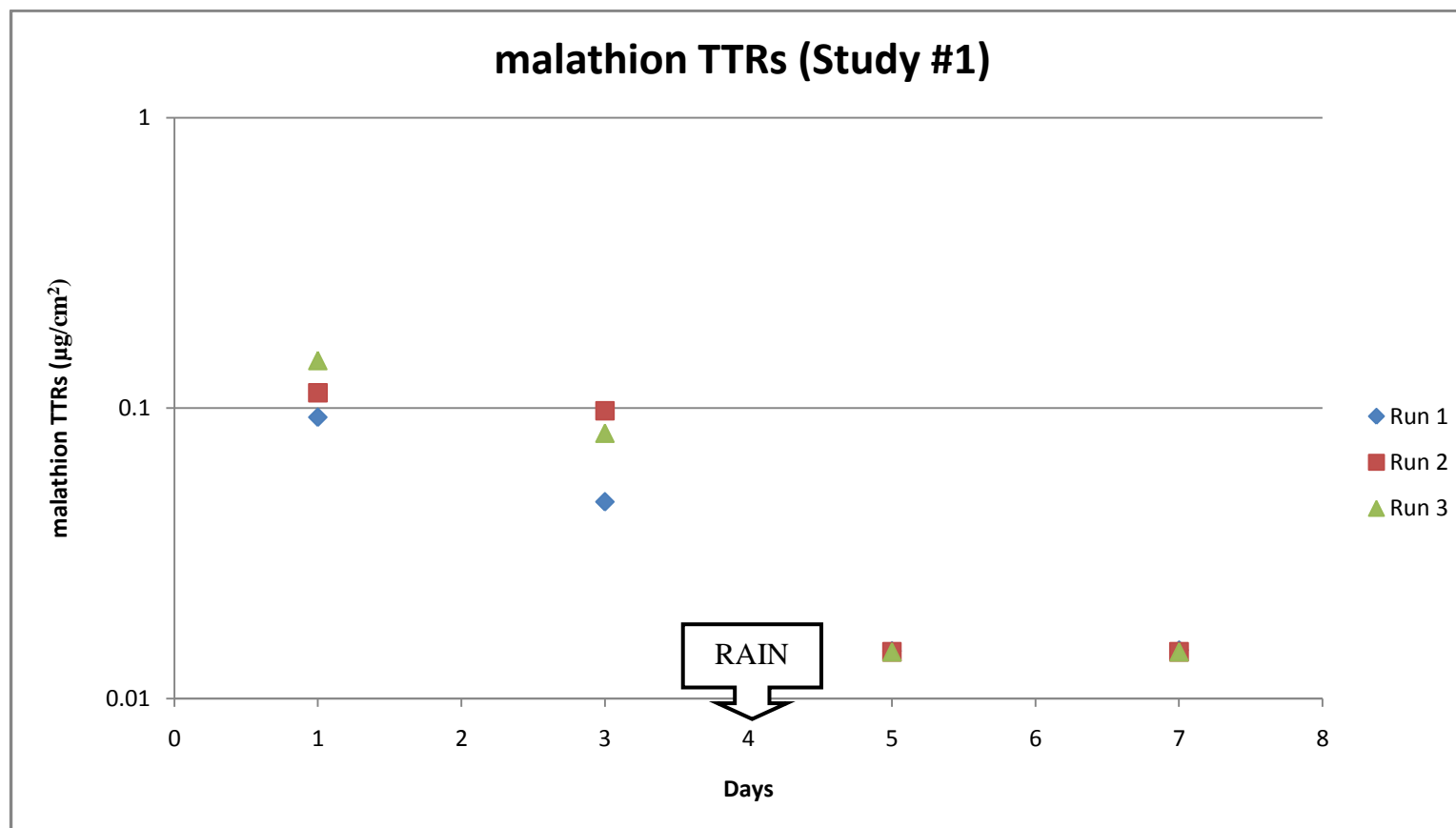


Figure 4.3: Malathion Transferrable Turf Residues (TTRs) for Study 1

Transferrable Turf Residues (TTRs) measured using 1500 cm² cotton cloth dosimeters and CDFA Roller on turf. Three samples were taken on each sampling day corresponding to a specific Run (designated sampling site area). A precipitation event occurred on Day 4. Effect of malathion washoff by rain is seen on Days 5 and 7.

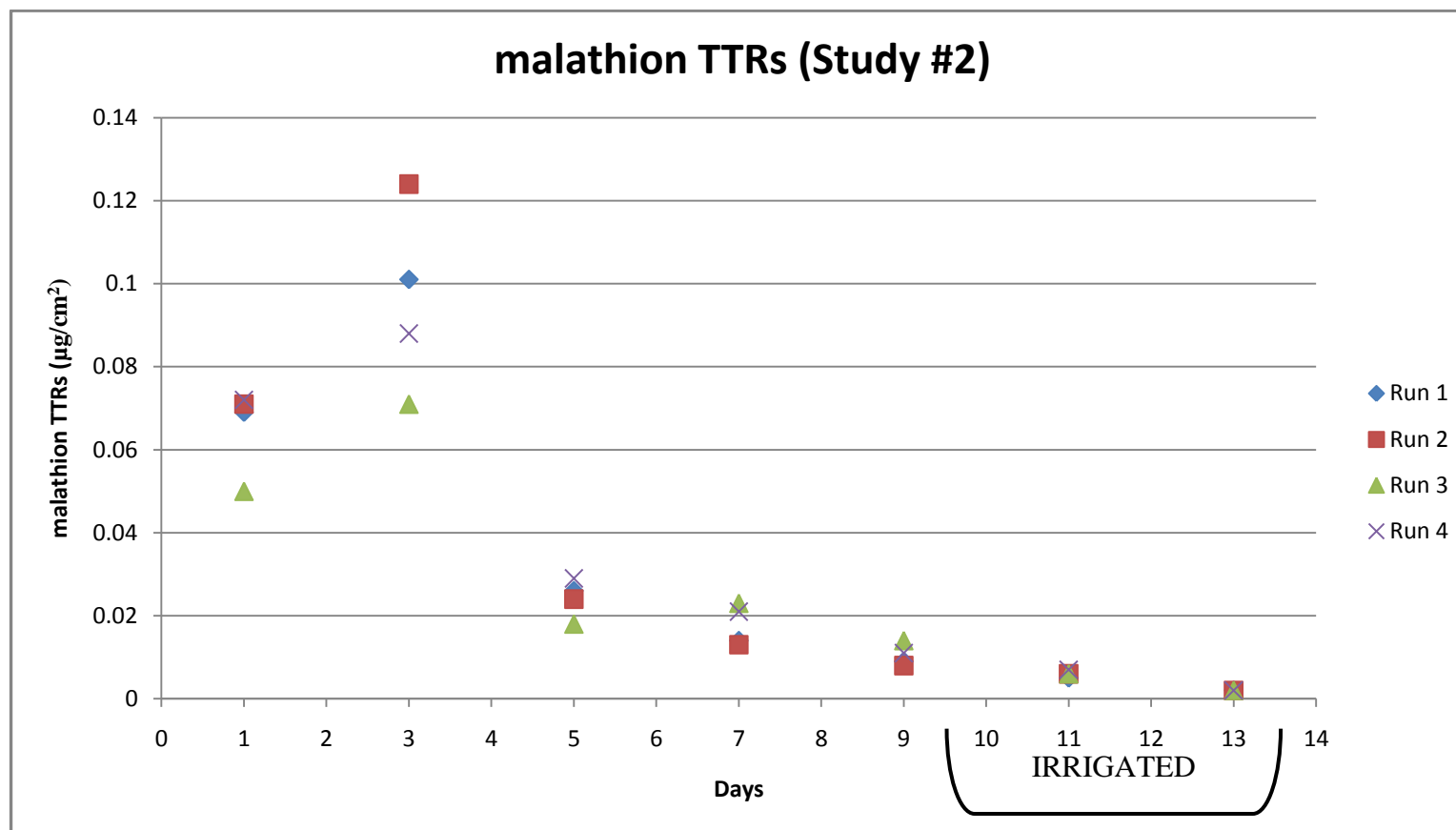


Figure 4.4: Malathion Transferrable Turf Residues (TTRs) for Study 2

Transferrable Turf Residues (TTRs) measured using 1500 cm² cotton cloth dosimeters and CDFA Roller on turf. Three samples were taken on each sampling day corresponding to a specific Run (designated sampling site area). Unexpected irrigation occurred from Days 10 to 13. Irrigation occurred early mornings (6 am) during those days.

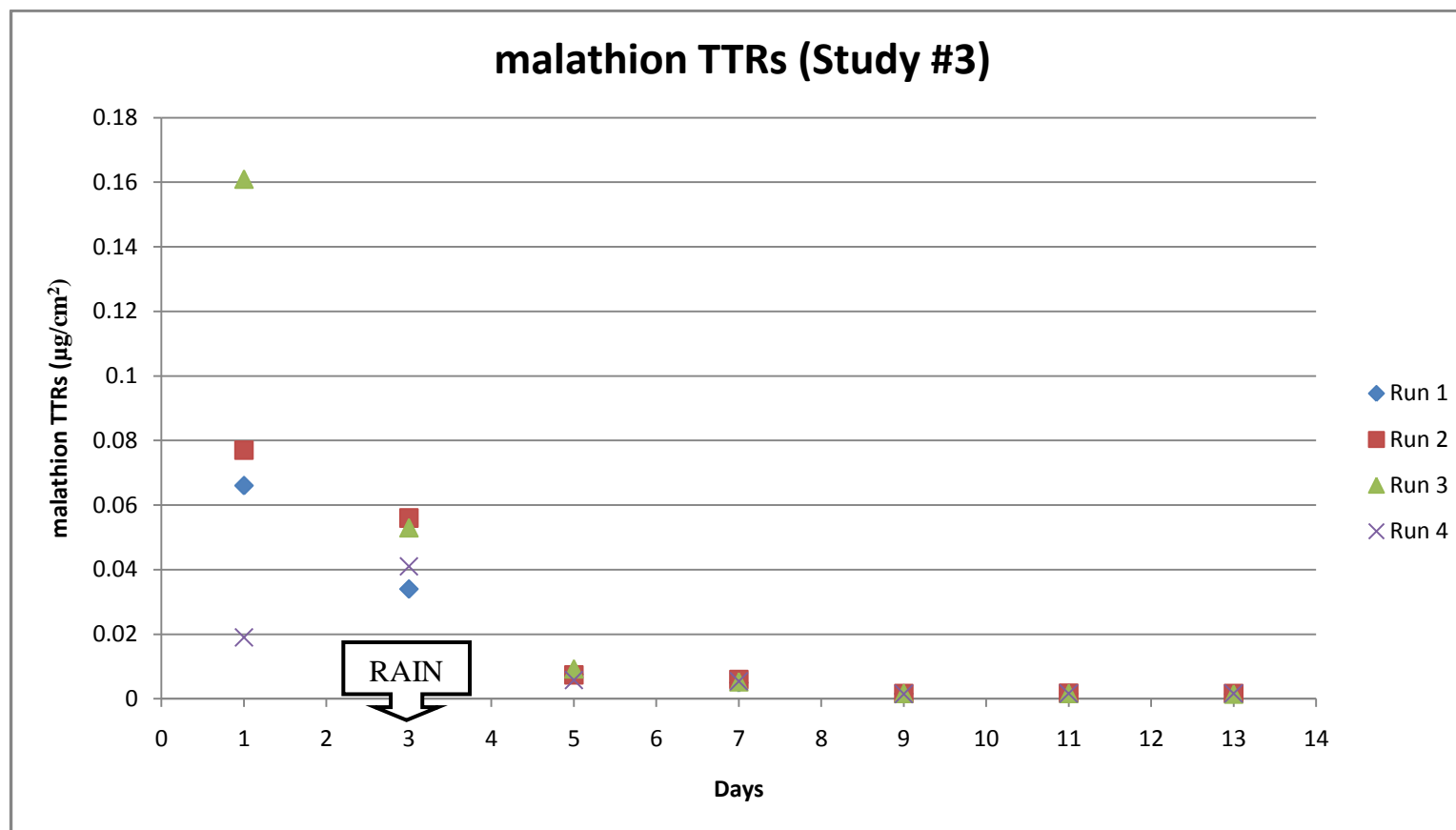


Figure 4.5: Malathion Transferrable Turf Residues (TTRs) for Study 3

Transferrable Turf Residues (TTRs) measured using 1500 cm² cotton cloth dosimeters and CDFA Roller on turf. Three samples were taken on each sampling day corresponding to a specific Run (designated sampling site area). A precipitation event occurred immediately after sampling on Day 3.

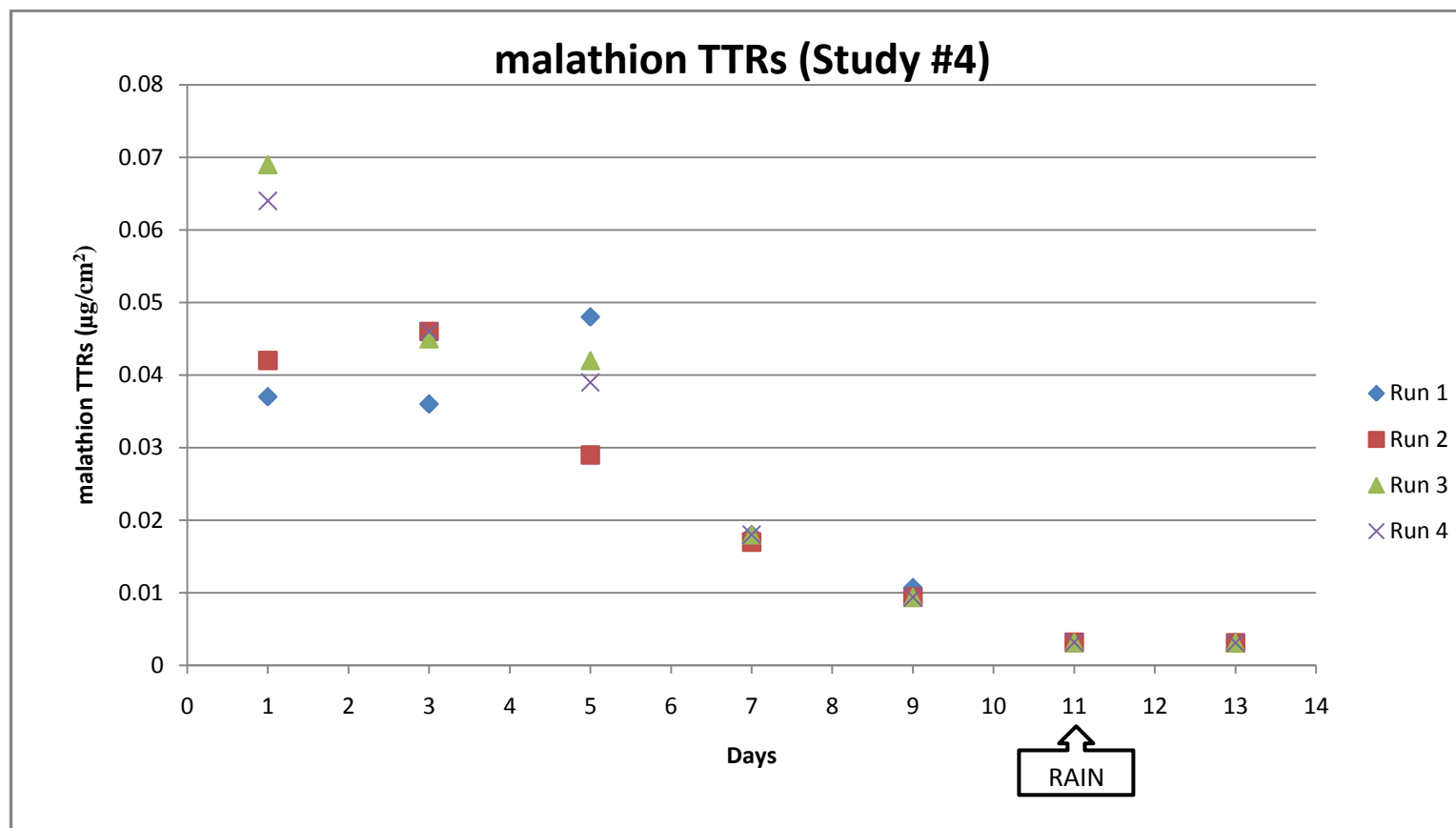


Figure 4.6: Malathion Transferrable Turf Residues (TTRs) for Study 4

Transferrable Turf Residues (TTRs) measured using 1500 cm² cotton cloth dosimeters and CDFA Roller on turf. Three samples were taken on each sampling day corresponding to a specific Run (designated sampling site area). Study #4 involves addition of an adjuvant (Activator 90®) in the spray mix. Precipitation event occurred on day 11.



Figure 4.7: Cotton Gloves Show Indicator Dye (Contact) on Fingers After “Run 1” Pass on Turf Using the BCTU



Figure 4.8: Cotton Gloves Show Indicator Dye (Contact) on Fingers After “Run 2” Pass on Turf Using the BCTU



Figure 4.9: Cotton Gloves Show Indicator Dye (Contact) on Fingers After “Run 3” Pass on Turf Using the BCTU



Figure 4.10: Cotton Gloves Show Indicator Dye (Contact) on Fingers After “Run 4” Pass on Turf Using the BCTU

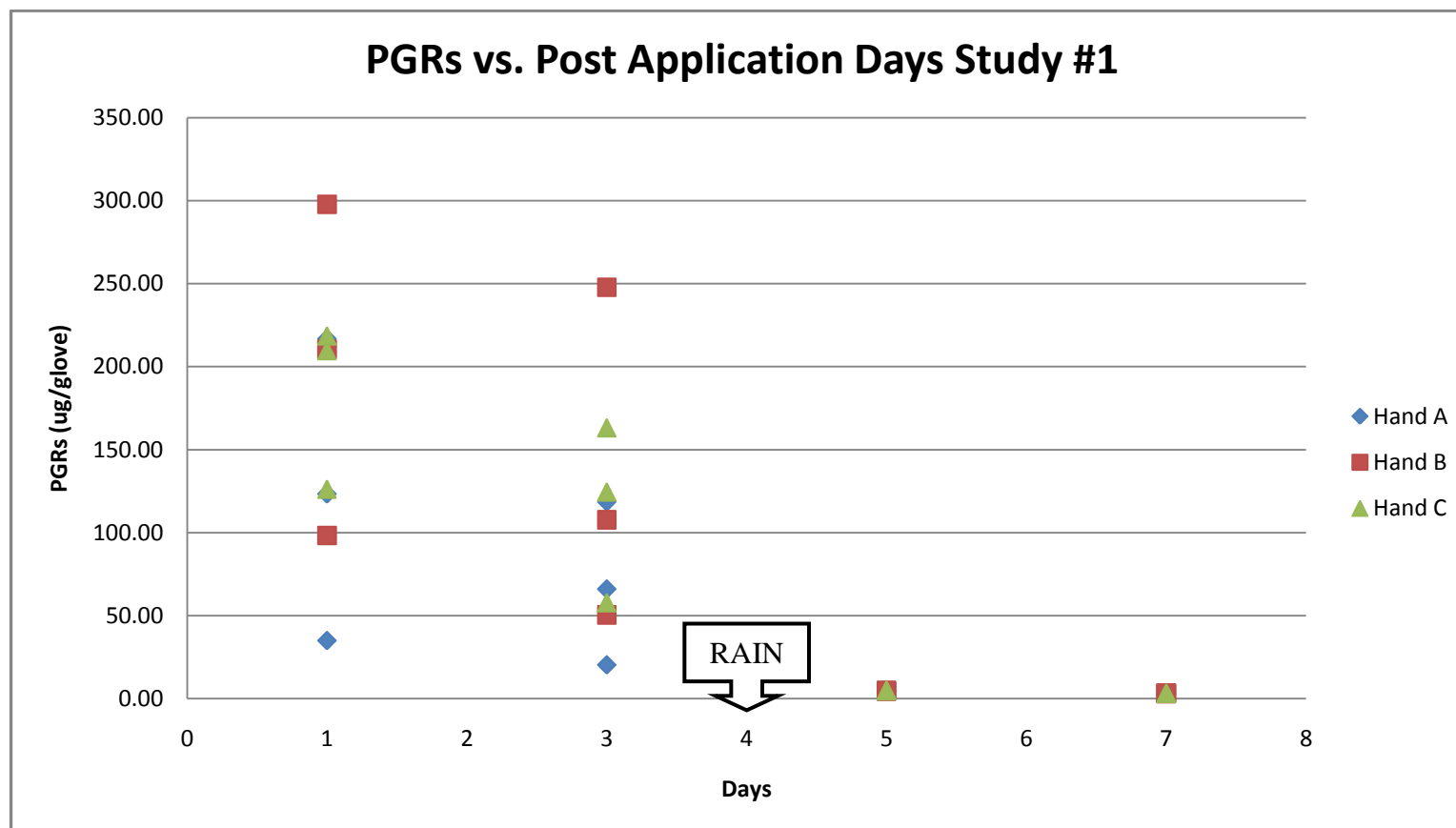


Figure 4.11: Pesticide Glove Residues (PGRs) Plotted Against Post Application Days for Study 1

Dissipation of malathion observed from each sampling hand (PGRs) from the BCTU over time. A precipitation event occurred on Day 4. Effect of malathion washoff by rain is seen on Days 5 and 7.

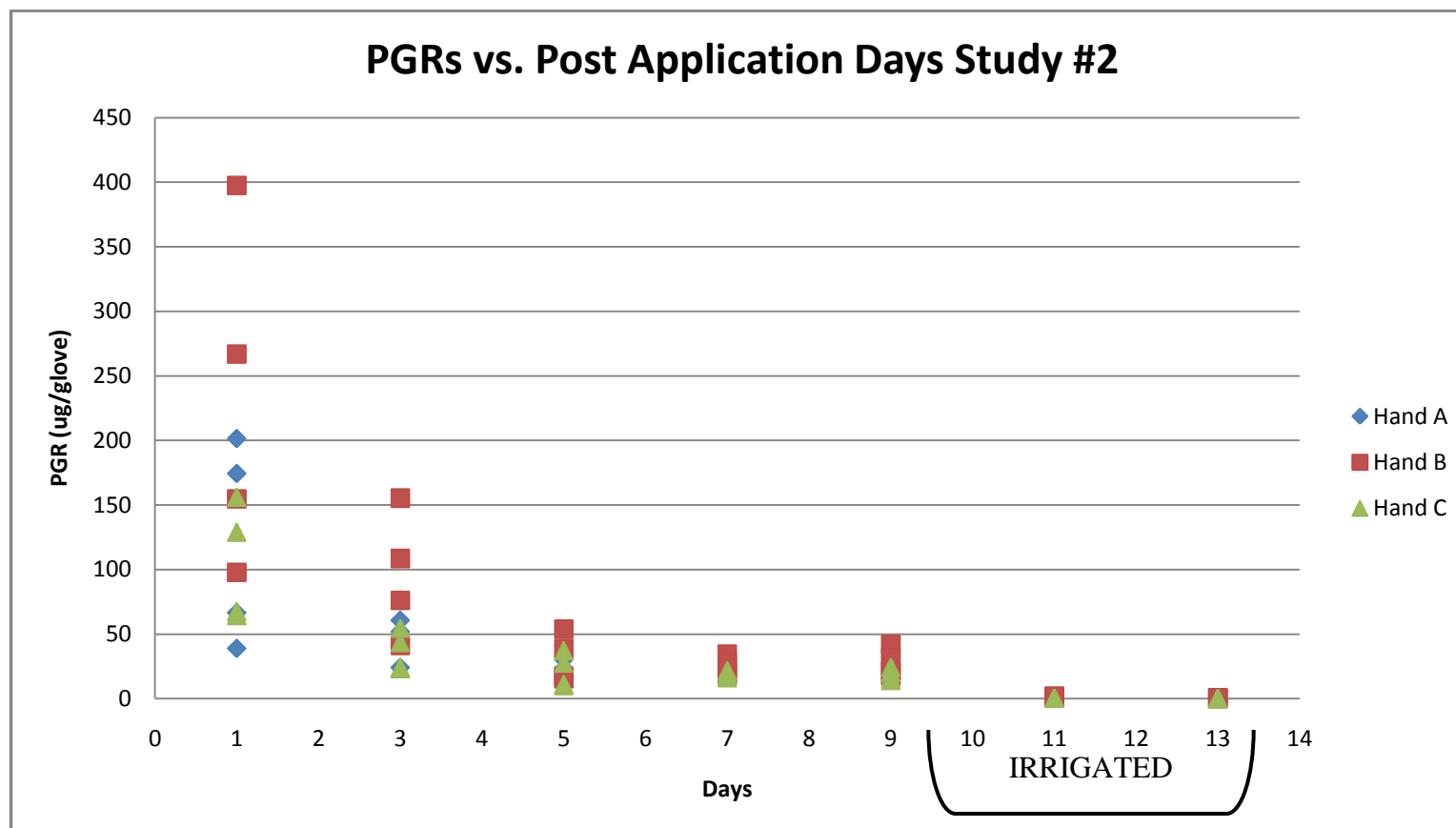


Figure 4.12: Pesticide Glove Residues (PGRs) Plotted Against Post Application Days for Study 2

Dissipation of malathion observed from each sampling hand (PGRs) from the BCTU over time. Unexpected irrigation occurred from Days 10 to 13. Irrigation occurred early mornings (6 am) during those days.

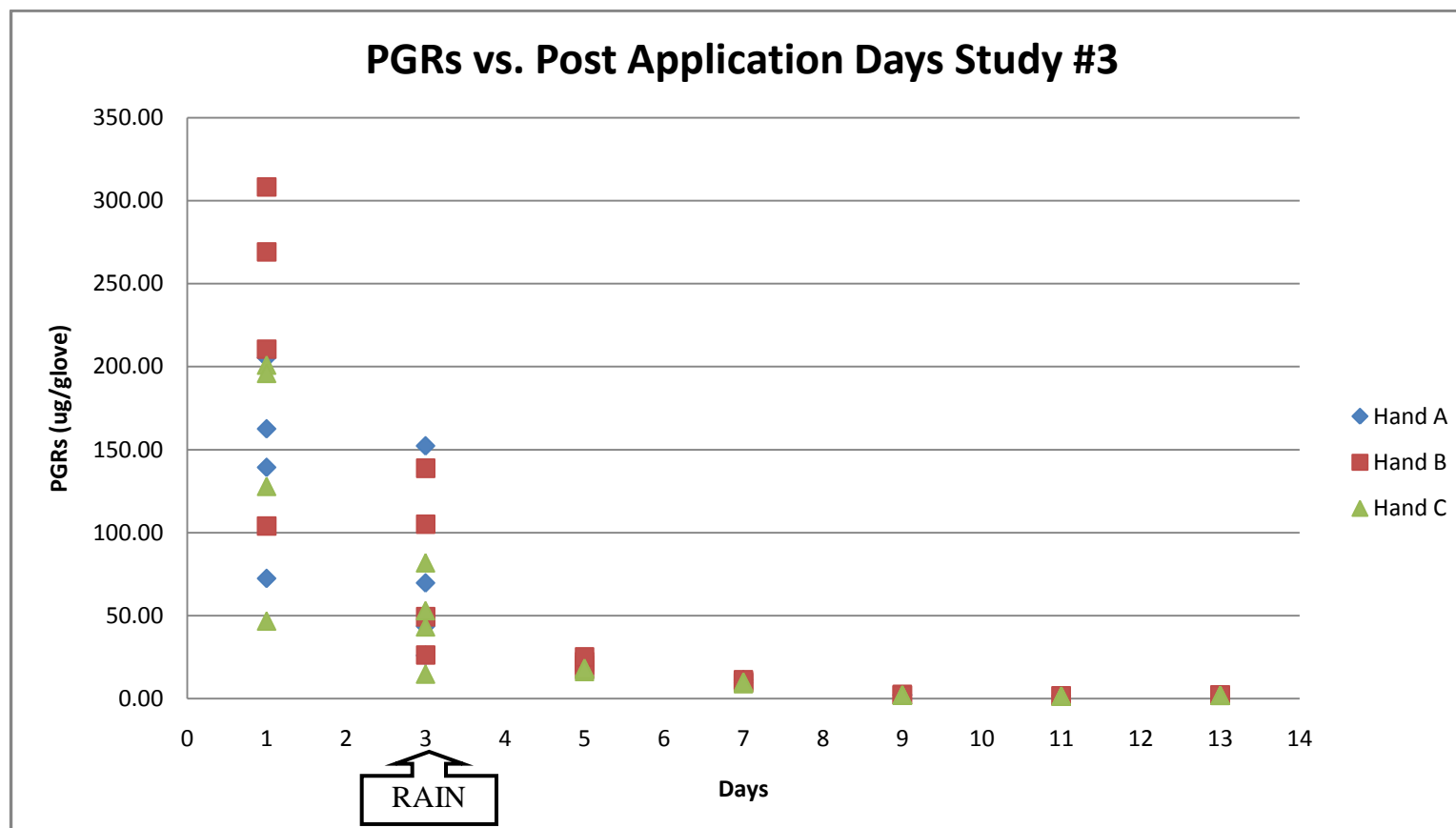


Figure 4.13: Pesticide Glove Residues (PGRs) Plotted Against Post Application Days for Study 3

Dissipation of malathion observed from each sampling hand (PGRs) from the BCTU over time. A precipitation event occurred immediately after sampling on Day 3.

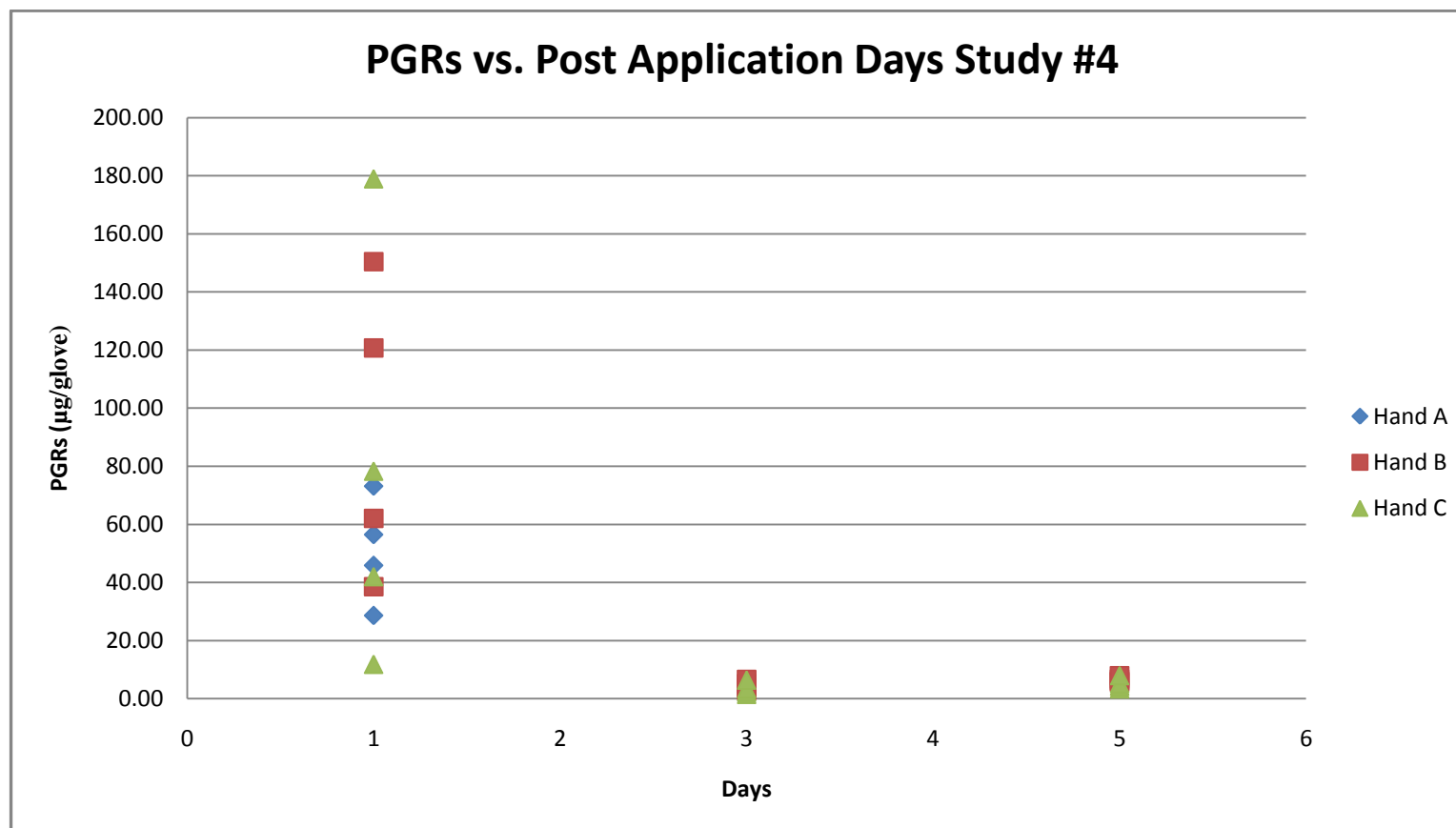


Figure 4.14: Pesticide Glove Residues (PGRs) Plotted Against Post Application Days for Study 4

Dissipation of malathion observed from each sampling hand (PGRs) from the BCTU over time. Study #4 involves addition of an adjuvant (Activator 90®) in the spray mix. Addition of adjuvant resulted in a decrease of pesticide residues transferred to gloves (PGRs).

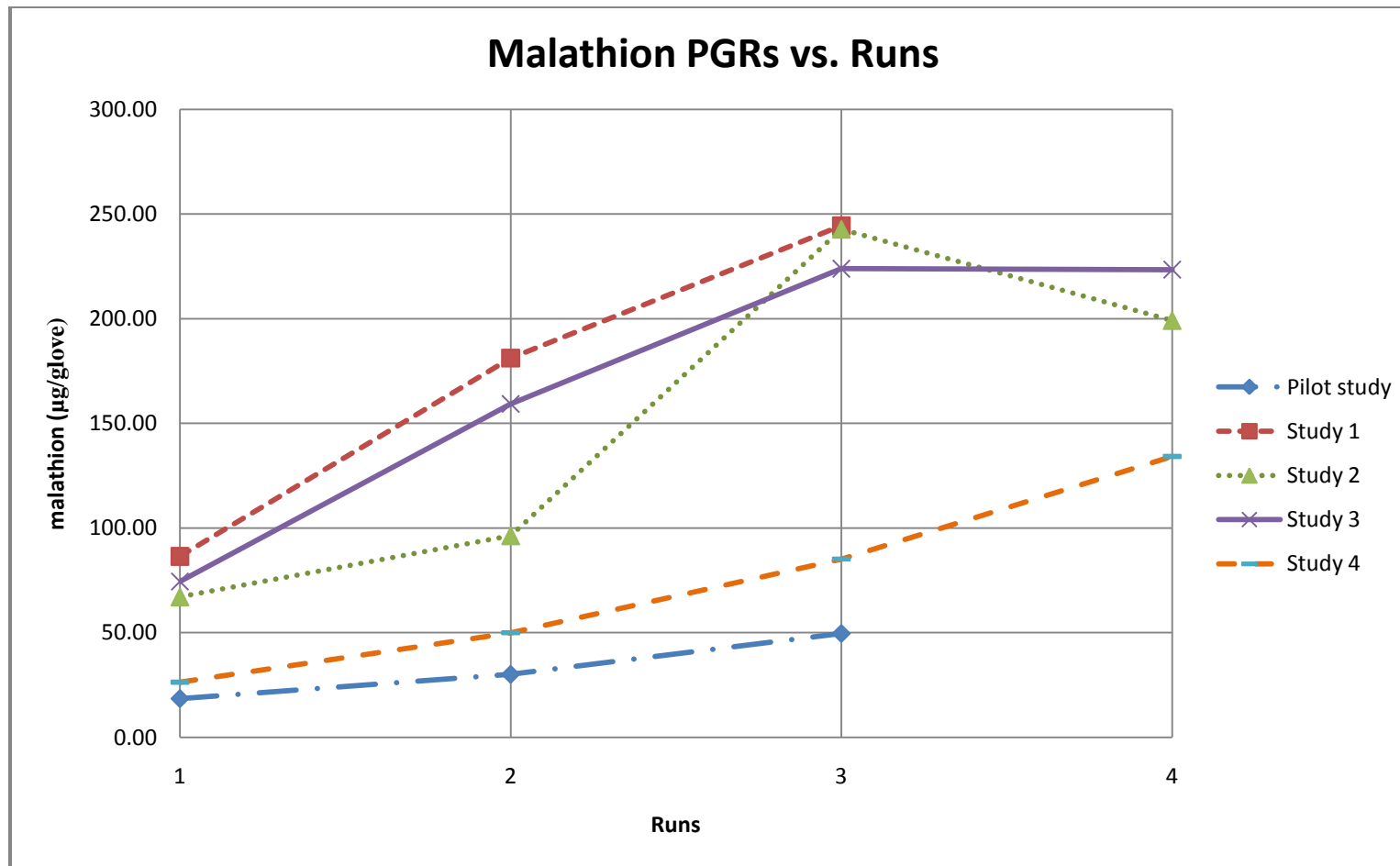


Figure 4.15: Malathion Pesticide Glove Residues (PGRs) Plotted Against Number of Runs From Each Study
 Malathion PGRs from Day 1 of each of the studies were plotted against Runs to determine the fate of the malathion residue on latex gloves after excessive contact with treated turf.

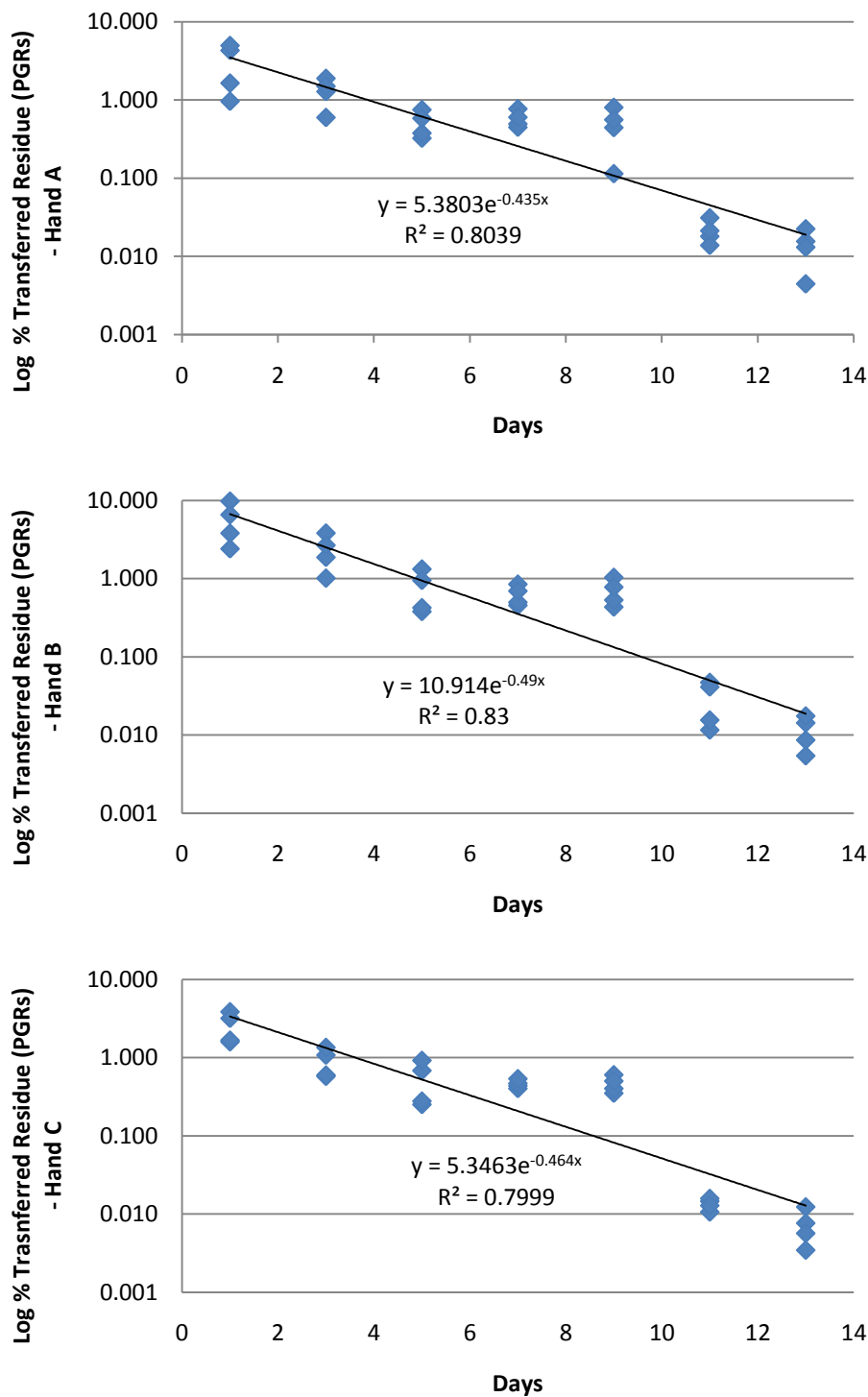


Figure 4.16: Percent Transferred Residue From Treated Turf to Gloves (Study 2)
 Study 2 had no interferences by rain or adjuvants therefore appropriately represented the percent transferred residue over time presented above from Hand A, B and C.

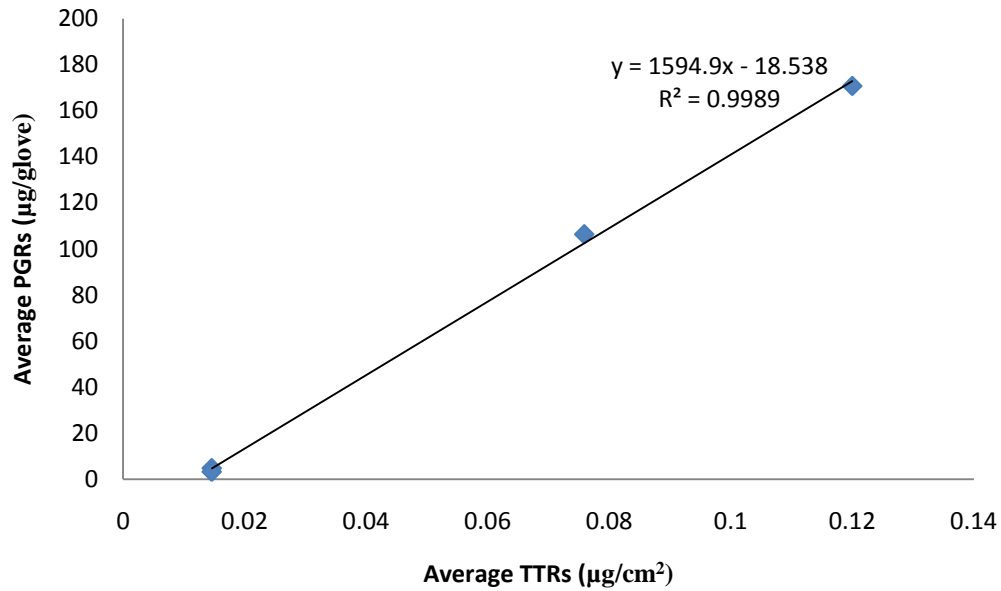


Figure 4.17: Correlation of Residue Transfer (BCTU vs. CDFA Roller) Study 1
PGRs (µg/glove) were plotted as a function of TTRs (µg/cm²). Each point represents a day in the study.

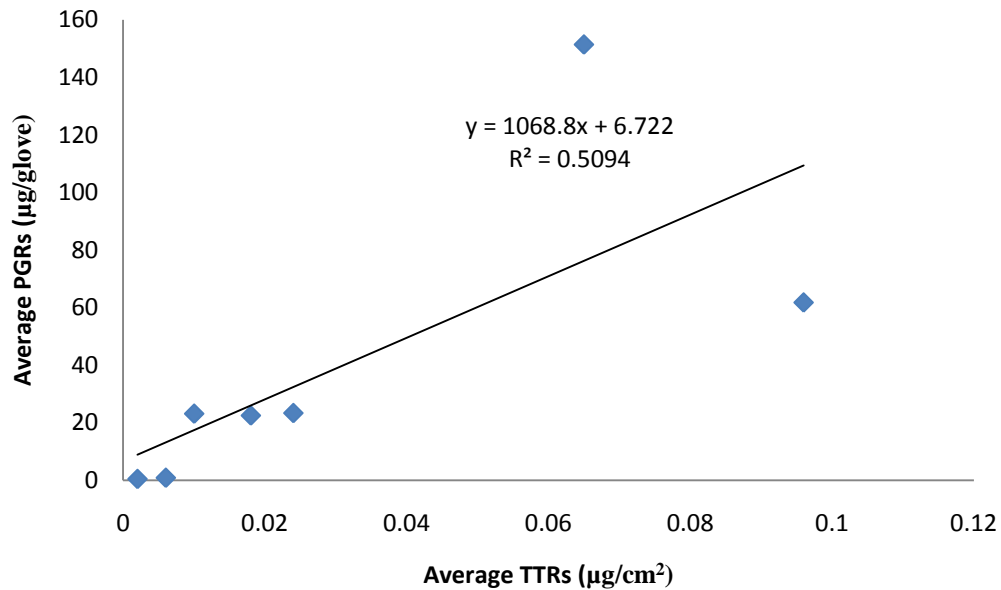


Figure 4.18: Correlation of Residue Transfer (BCTU vs. CDFA Roller) Study 2
PGRs (µg/glove) were plotted as a function of TTRs (µg/cm²). Each point represents a day in the study.

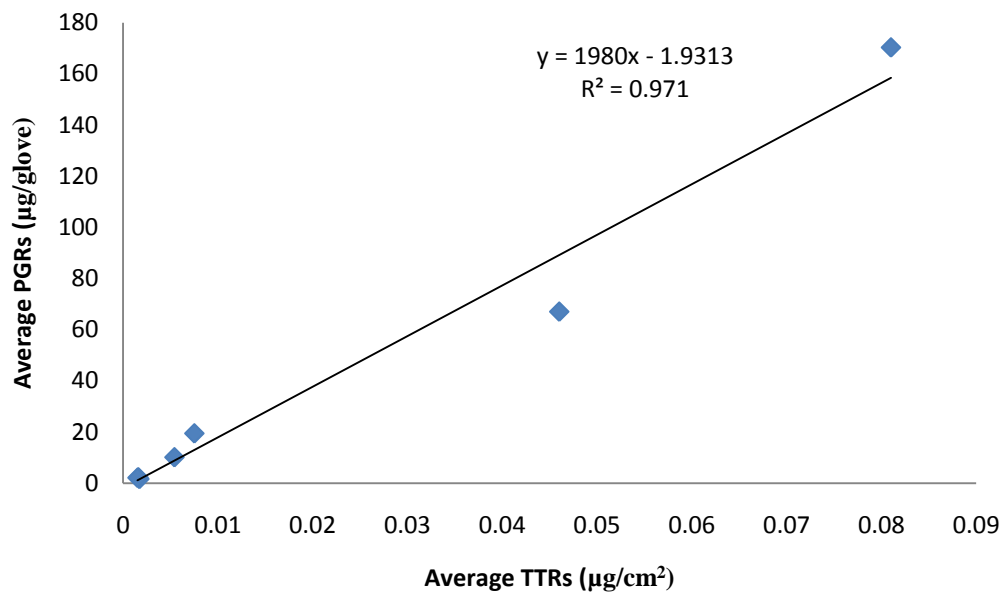


Figure 4.19: Correlation of Residue Transfer (BCTU vs. CDFA Roller) Study 3
PGRs (µg/glove) were plotted as a function of TTRs (µg/cm²). Each point represents a day in the study.

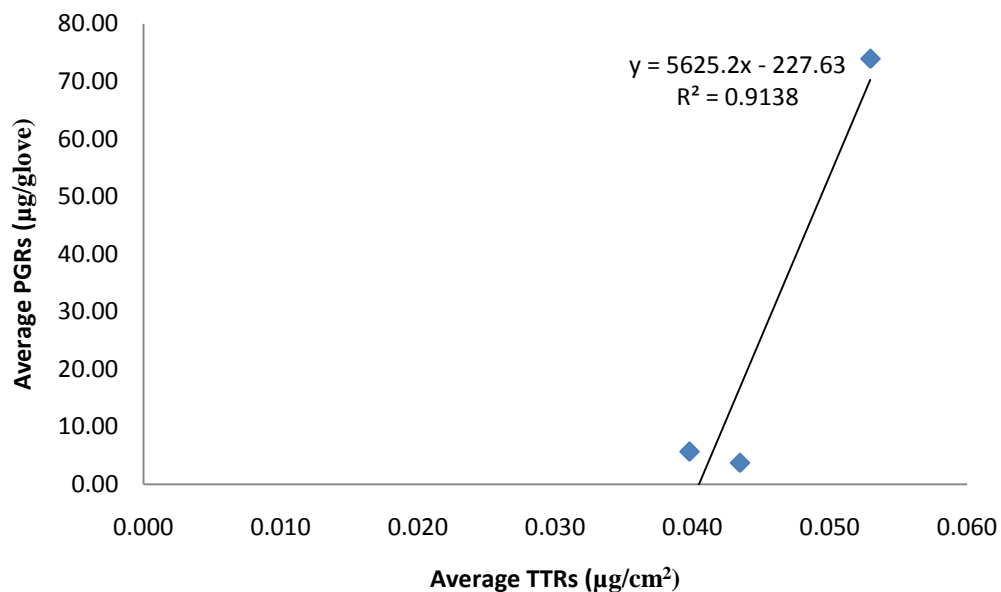


Figure 4.20: Correlation of Residue Transfer (BCTU vs. CDFA Roller) Study 4
PGRs (µg/glove) were plotted as a function of TTRs (µg/cm²). Each point represents a day in the study.

CHAPTER 5: CONCLUSIONS

5.1 Conclusion

Hands are an important route of dermal exposure to agricultural pesticides during strawberry harvesting (Krieger et al., 1991). They accounted for 60% to 90% of the total dermal exposure measured using cotton glove dosimeters in fields treated with captan, carbaryl, vinclozolin, and benomyl (U.S. EPA, 1980-1986). Latex gloves as hand dosimeters for exposure estimates have been evaluated in two settings: 1) on commercial strawberry farms and 2) in controlled studies using a surrogate contact transfer device and malathion-treated turf.

Pesticide Glove Residues on a Commercial Strawberry Farm

Rubber latex gloves of harvesters on a commercial strawberry farm accumulated multiple pesticide residues during normal work periods (2 to 2.5 h). A total of 13 different pesticide parent compounds were found on harvester gloves at different times. Pesticide residues can accumulate on rubber latex gloves up to ~20 mg/pair (captan fungicide) by intermittent contact.

Spray records were used to evaluate the dissipation of residues lacking actual field residue measurements or biomonitoring data. The results of the glove residue studies were much more inconsistent than expected. Spray records do not provide specific spray data concerning the timing and location of spray events. A need for controlled applications and repeated sampling by particular harvesters may be necessary to obtain more consistent and less variable data.

Evaluation of Rubber Latex Gloves as a Direct Dosimeter

A surrogate contact-transfer device was used to measure malathion uptake from treated turf. The device consisted of latex gloves fitted on mannequin hands mounted in a wheeled chassis, the Brinkman Contact Transfer Unit (BCTU), that could be pushed across a grid of treated turf. The residue is transferred from treated turf by continuous contact during a defined set of runs (time) whereas contact transfer to gloves worn by strawberry harvesters is intermittent contact during 2 to 2.5 h work periods.

The accumulation of pesticide residues on gloves was dependent on the extent of contact to treated foliage. The percent malathion transferred residue from treated turf to a gloved mannequin hand (assuming 420 cm² surface area) ranged from <1% to 10% based on measurements of deposition applied to turf. Latex glove dosimeters also accumulated multiple pesticide residues as determined by concurrent applications of malathion and fenpropathrin (data not shown) to turf. Residues dissipated biphasically over a 13 d study period. First order pesticide glove residue (PGR) half-lives were approximately 1.4 d for malathion and 4.6 d for fenpropathrin. Both insecticides were highly susceptible to wash-off by rain and the amount of transferrable residue was also affected by the addition of an adjuvant (Activator 90[®]) in the tank mix.

Transferable turf residues (TTRs) were also measured using the CDFFA (California) roller and cotton cloth dosimeters. Residues accumulated on cotton cloths (TTRs: 0.002 -0.117 µg /cm²) were less than the amounts accumulated on gloves (PGRs: 0.14 – 398 µg/glove or 0.0003-0.95 ug/cm² assuming a 420 cm² total glove surface area). When plotting PGRs (µg/glove) and TTRs (µg/cm²), a strong linear regression

correlation was observed ($R^2 = 0.5 - 1.0$) indicating that the residue transfer was consistent over time by both contact transfer methods (BCTU and CDFA roller). An empirical transfer factor of $1548 \text{ cm}^2/\text{glove}$ was derived from the resulting slope when plotting PGRs as a function of TTRs. This empirical transfer factor approximates residue transfer estimates in cm^2/glove by contact transfer methods (using the BCTU and CDFA roller). Additional studies are required to clarify this transfer factor.

A primary limitation to using the BCTU for surrogate dermal monitoring was not being able to sample for extended periods of time. Thus inhibiting the amount of contact the gloves can come to treated foliage. Relatively large amounts of treated turf are required for single experiments and variability is high due to environmental factors that are difficult to assess and control (i.e. condition of the turf, weather, moisture etc.).

Appendix 1: Instruction Sheet Provided to DB Specialty Farms Field Operators

Instruction for Glove Collections

First, thanks for helping us collect gloves. We would like you to start by collecting 7 sets of gloves (from collection 1 to collection 7). Additional gloves will be supplied as needed. Please collect 10 pairs of gloves for each set. We provide labeled Ziploc bags for you to contain gloves. There are total 7 big gallon-sized Ziploc bags. Each big bag contains 10 small quart-sized Ziploc bags. The big bags were labeled from collection 1 to collection 7. Please use one for each collection. Please follow the details for glove collection:

- Please write the collection date on the label which is on the big gallon-sized bag; please also write the date on the data sheet: "GLOVE COLLECTION RECORD".
- Please collect gloves at the **LUNCH BREAK**.
- Please randomly collect 10 pairs of gloves from 10 harvesters.
- Please ask the harvesters to put their gloves directly into the small quart-sized ZipLock bags.
- Please put the 10 small bags containing gloves into the big Ziploc bag.
- Please transfer the big bag containing gloves to an ice chest containing frozen blue ice.
- Please store the gloves in the UCR Freezer in your office.
- Please contact us if you have any questions about the glove collection and storage:

Gayatri Sankaran : gayatri.sankaran@email.ucr.edu

(Office): 951-827-4424

(Mobile): 951-231-0347

Bob Krieger: bob.krieger@ucr.edu

(Office): 951-827-3724

Thanks a lot for all of your time and invaluable help!

Personal Chemical Exposure Program
University of California, Riverside

Appendix 2: CDFA Roller Specifications and Experimental Protocol

Materials Required: 30 lb CDFA roller, cotton cloth dosimeter (50cm x 30cm), aluminum foil and roller screen with frame.

CDFA Roller Specifications:

Weight: 30 lbs
Length: 2 feet (sampling distance)
Diameter: 4 inches
Handle: ~24 inches

Dosimeters:

100% white cotton cloth
1500 cm² cotton cloth sheet
Heavy duty aluminum sheets to cover cloth during sampling
Frame with screen to hold sheets in place during sampling

Experimental Protocol:

1. Wearing a clean pair of gloves, carefully place the cotton sheet on the sampling plot (do not adjust the location once it touches the turf).
2. Place a large sheet of heavy duty foil paper to cover the entire cotton cloth.
3. Place the roller screen over the aluminum foil.
4. Apply downward pressure to the frame of the screen by firmly pressing down on all four corners (assistance of 2 people are needed).
5. Gently place the CDFA roller on the sampling assembly.
6. Gently and evenly, with no downward pressure applied to the roller, move the roller over the assembly 20 times to capture transferable residues. (Note: one forward and backward motion is considered one roll).
7. After rolling, the roller is picked up and taken to a clean area to prevent contamination.
8. Remove the rolling screen and discard the aluminum foil.
9. Then lift the cloth from the turf.
10. Gently fold the cotton sheet in the middle so that the side that contacted the turf is together.
11. Place the cotton sheet in an appropriately labeled quart sized zip-lock bag for transport back to lab.

Appendix 3: The Brinkman Contact Transfer Unit (BCTU) Specifications and Experimental Protocol

Materials Required: powder free rubber latex gloves, rubber bands, BCTU

BCTU Specifications:

Length of handle: 43.5''
Width of handle: 15.5''
Width of chassis (front wheel to front wheel): 21.5''
Length of chassis (back wheel to front wheel): 32''
Center cut hexagon (inner chassis) side length: 14''
Center cut hexagon (inner chassis) sides: 9''
Diameter of wheels: 7''
Chassis height to ground level: 5.5''

Mannequin Hands Specifications:

Length of arm: 5''
Wrist to middle finger: 7''
Wrist to index finger: 6.5''
Wrist to thumb: 4.78''
Wrist to ring finger: 6.5''
Wrist to pinky finger: 5.25''
Knuckle length: 3''
Wrist width: 2.25''

Experimental Protocol:

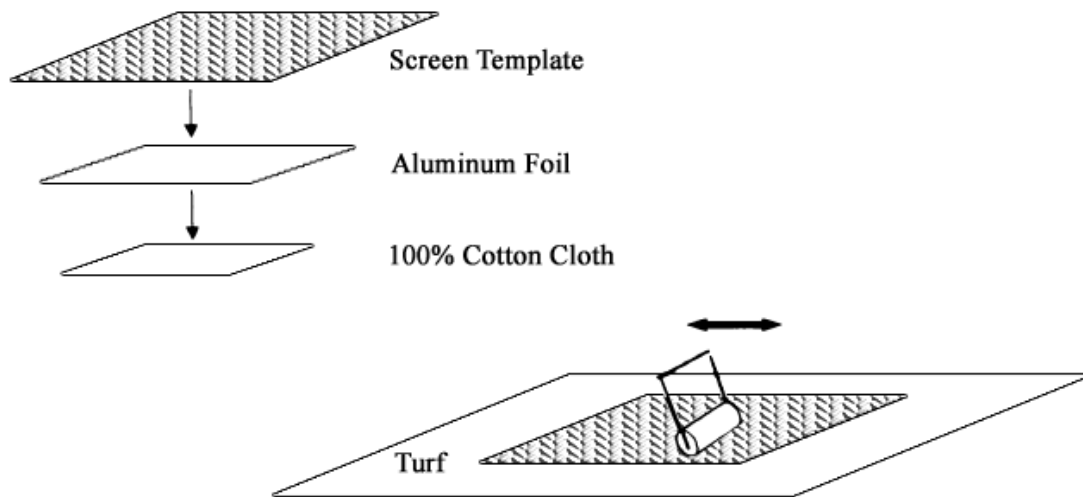
1. Make sure the BCTU lever is in the upright position.
2. While wearing a clean pair of gloves, place a single powder free rubber latex glove on each of the mannequin hands (hands A, B, and C).
3. Wrap a rubber band around the wrist of each mannequin hand to hold the rubber latex gloves in place.
4. Position the BCTU at the left corner of the lane.
5. Remove the pin placed on the lever that holds the mannequin hands in the upright position and lower the lever so that the hands contact the turf.
6. To push the BCTU along it is suggested to place hands underneath the handle bars rather than over since the BCTU is light in weight and the front wheels can easily be lifted off the turf if not careful.
7. Push the BCTU along the left side length of the row ONLY.

8. Once the front wheels pass the END flags, lift the lever so that the hands are in the upright position.
9. Pivot on the back wheels to make a sharp turn back into the same lane.
10. Repeat steps 4-9 for the intended number of runs.
11. Passing the END flags on the last pass of the final lane, lift the lever so that the mannequin hands are in the upright position
12. Place the holding pin on the lever back into place.
13. With clean gloves, slide the rubber bands holding the rubber latex gloves in place and remove each glove by pinching the glove from the top surface of the mannequin hands.
14. Place each individual rubber latex glove sample from a single mannequin hand into a properly labeled quart sized Zip-lock bag.
15. Transport back to lab for extraction of pesticide residues from the rubber latex gloves.

Appendix 4: Pictures of the Brinkman Contact Transfer Unit (BCTU)



Appendix 5: CDFA Roller Diagram (Williams, 2000) and Picture



Appendix 6: Malathion 8 Aquamul® Label



MALATHION 8 AQUAMUL

Organophosphate Insecticide

ACTIVE INGREDIENT:		BY WT.
Malathion (O,O-Dimethyl phosphorodithioate of diethyl mercaptosuccinate)	81.8%	
INERT INGREDIENTS:	18.2%	
	TOTAL	100.0%

Contains 8 lbs. Malathion per gallon.

KEEP OUT OF REACH OF CHILDREN
CAUTION

FIRST AID

If swallowed:	<ul style="list-style-type: none">• Call a poison control center or doctor immediately for treatment advice.• Have a person sip a glass of water if able to swallow.• Do not induce vomiting unless told to do so by the poison control center or doctor.• Do not give anything by mouth to an unconscious person.
If inhaled:	<ul style="list-style-type: none">• Move person to fresh air.• If person is not breathing, call 911 or an ambulance, then give artificial respiration, preferably by mouth-to-mouth, if possible.• Call a poison control center or doctor for further treatment advice.
If on skin or clothing:	<ul style="list-style-type: none">• Take off contaminated clothing.• Rinse skin immediately with plenty of water for 15-20 minutes.• Call a poison control center or doctor for treatment advice.
If in eyes:	<ul style="list-style-type: none">• Hold eye open and rinse slowly and gently with water for 15-20 minutes.• Remove contact lenses, if present, after the first 5 minutes, then continue rinsing eye.• Call a poison control center or doctor for treatment advice.

Note to Physician: This product may cause cholinesterase inhibition. Atropine is antidotal. 2-PAM may be effective as an adjunct to atropine.

FOR A MEDICAL EMERGENCY INVOLVING THIS PRODUCT CALL: 1-866-944-8565.

Have the product container or label with you when calling a poison control center or doctor, or going for treatment.

DO NOT USE, POUR, SPILL, OR STORE NEAR HEAT OR OPEN FLAME.

See Below For Additional Precautionary Statements

EPA REG. NO. 34704-474

EPA EST. NO. 34704-MS-002

NET CONTENTS 2½ GALS. (9.46 L)

CYTHION

IHT

051704 V4D 08Y09

MALATHION 8 AQUAMUL
EPA REG. NO. 34704-474

**PRECAUTIONARY STATEMENTS HAZARDS TO
HUMANS AND DOMESTIC ANIMALS CAUTION**

Harmful if swallowed or absorbed through skin. Causes moderate eye irritation. Avoid contact with eyes, skin, or clothing. Prolonged or frequently repeated skin contact may cause allergic reaction in some individuals.

Personal Protective Equipment:

Applicators and other handlers must wear:

- Long-sleeved shirt and long pants,
- Chemical-resistant gloves, such as barrier laminate, butyl rubber, nitrile rubber or viton,
- Shoes plus socks and
- Protective eyewear.

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

Engineering controls statements:

When handlers use closed systems, enclosed cabs, or aircraft in a manner that meets with 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.

ENVIRONMENTAL HAZARDS

This pesticide is toxic to fish, aquatic invertebrates, and aquatic life stages of amphibians. For terrestrial uses, do not apply directly to water, or to areas where surface water is present or to intertidal areas below the mean high water mark. Drift and runoff may be hazardous to aquatic organisms in areas near the application site. Do not contaminate water when disposing of equipment washwaters.

This product is highly toxic to bees exposed to direct treatment on blooming crops or weeds. Do not apply this product or allow it to drift to blooming crops or weeds if bees are visiting the treatment area.

PHYSICAL & CHEMICAL HAZARDS

Do not use or store near heat or open flame.

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.

MALATHION 8 AQUAMUL
EPA REG. NO. 34704-474

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,
- Chemical-resistant gloves, such as barrier laminate, butyl rubber, nitrile rubber or viton,
- Shoes plus socks and
- Protective eyewear.

**APPLICATION THROUGH IRRIGATION SYSTEMS-
CHEMIGATION**

Apply this product only through sprinkler, including center pivot, lateral move, end tow, side (wheel) roll, traveler, big gun, solid set, or hand move; flood (basin); furrow; border; or drip (trickle) irrigation systems. Do not apply this product through any other type of irrigation system.

Crop injury, lack of effectiveness, or illegal pesticide residues in the crop can result from nonuniform distribution of treated water.

If you have questions about calibration, you should contact State Extension Service specialists, equipment manufacturers or other experts.

Do not connect an irrigation system (including greenhouse systems) used for pesticide application to a public water system unless the pesticide label-prescribed safety devices for public water systems are in place.

A person knowledgeable of the chemigation system and responsible for its operation, or under the supervision of the responsible person, shall shut the system down and make necessary adjustments should the need arise.

Mix in clean supply tank the recommended amount of this product for acreage to be covered, and needed quantity of water.

This product should not be tank-mixed with other pesticides, surfactants or fertilizers unless prior use has shown the combination noninjurious under your conditions of use.

Follow precautionary statements and directions for all tank-mixed products.

On all crops, use sufficient gallonage of water to obtain thorough and uniform coverage, but not cause runoff or excessive leaching. This will vary depending on equipment, pest problem and stage of crop growth. Application of more or less than optimal quantity of water may result in decreased chemical performance, crop injury or illegal pesticide residues.

MALATHION 8 AQUAMUL
EPA REG. NO. 34704-474

Meter this product into the irrigation water uniformly during the period of operation. Do not overlap application. Follow recommended label rates, application timing, and other directions and precautions for crop being treated.

Continuous mild agitation of pesticide mixture may be needed to assure a uniform application, particularly if the supply tank requires a number of hours to empty.

CHEMIGATION SYSTEMS CONNECTED TO PUBLIC WATER SYSTEMS

Note: Loveland Products Inc., does not encourage connecting chemigation systems to public water supplies. The following information is provided for users who have diligently considered all other application and water supply options before electing to make such a connection.

Public water system means a system for the provision to the public of piped water for human consumption if such system has at least 15 service connections or regularly serves an average of at least 25 individuals daily at least 60 days out of the year. Chemigation systems connected to public water systems must contain a functional, reduced-pressure zone, backflow preventer (RPZ) or the functional equivalent in the water supply line upstream from the point of pesticide introduction. As an option to the RPZ, the water from the public water system should be discharged into a reservoir tank prior to pesticide introduction. There shall be a complete physical break (air gap) between the outlet end of the fill pipe and the top or overflow rim of the reservoir tank of at least twice the inside diameter of the fill pipe.

The pesticide injection pipeline must contain a functional, automatic, quick-closing check valve to prevent the flow of fluid back toward the injection pump.

The pesticide injection pipeline must contain a functional, normally closed, solenoid-operated valve located on the intake side of the injection pump and connected to the system interlock to prevent fluid from being withdrawn from the supply tank when the irrigation system is either automatically or manually shut down.

The system must contain functional interlocking controls to automatically shut off the pesticide injection pump when the water pump motor stops, or in cases where there is no water pump, when the water pressure decreased to the point where pesticide distribution is adversely affected.

Systems must use a metering pump, such as a positive displacement injection pump (e.g., diaphragm pump) effectively designed and constructed of materials that are compatible with pesticides and capable of being fitted with a system interlock.

Do not apply when wind speed favors drift beyond the area intended for treatment.

SPRINKLER CHEMIGATION (FOLIAR SPRAY USES)

The system must contain a functional check valve vacuum relief valve, and low pressure drain appropriately located on the irrigation pipeline to prevent water source contamination from backflow.

The pesticide injection pipeline must contain a functional, automatic, quick-closing check valve to prevent the flow of fluid back toward the injection pump.

The pesticide injection pipeline must also contain a functional, normally closed, solenoid-operated valve located on the intake side of the injection pump and connected to the system interlock to prevent fluid from being withdrawn from the supply tank when the irrigation system is either automatically or manually shut down.

The system must contain functional interlocking controls to automatically shut off the pesticide injection pump when the water pump motor stops.

**MALATHION 8 AQUAMUL
EPA REG. NO. 34704-474**

The irrigation line or water pump must include a functional pressure switch which will stop the water pump motor when the water pressure decreases to the point where pesticide distribution is adversely affected.

Systems must use a metering pump, such as a positive displacement injection pump (e.g., diaphragm pump) effectively designed and constructed of materials that are compatible with pesticides and capable of being fitted with a system interlock.

Do not apply when wind speed favors drift beyond the area intended for treatment.

FLOOD (BASIN), FURROW AND BORDER CHEMIGATION (SOIL DRENCH USES)

Systems using a gravity flow pesticide dispensing system must meter the pesticide into the water at the head of the field and downstream of a hydraulic discontinuity such as a drop structure of weir box to decrease potential for water source contamination from backflow if water flow stops.

Systems utilizing a pressurized water and pesticide injection system must meet the following requirements:

- a. The system must contain a functional check valve, vacuum relief valve, and low pressure drain appropriately located on the irrigation pipeline to prevent water source contamination from backflow.
- b. The pesticide injection pipeline must contain a functional, automatic, quick-closing check valve to prevent the flow of fluid back toward the injection pump.
- c. The pesticide injection pipeline must also contain a functional, normally closed, solenoid-operated valve located on the intake side of the injection pump and connected to the system interlock to prevent fluid from being withdrawn from the supply tank when the irrigation system is either automatically or manually shut down.
- d. The system must contain functional interlocking controls to automatically shut off the pesticide injection pump when the water pump motor stops.
- e. The irrigation line or water pump must include a functional pressure switch which will stop the water pump motor when the water pressure decreases to the point where pesticide distribution is adversely affected.
- f. Systems must use a metering pump, such as a positive displacement injection pump (e.g., diaphragm pump) effectively designed and constructed of materials that are compatible with pesticides and capable of being fitted with a system interlock.

DRIP (TRICKLE) CHEMIGATION (SOIL DRENCH USES)

The system must contain a functional check valve, vacuum relief valve and low pressure drain appropriately located on the irrigation pipeline to prevent water source contamination from backflow.

The pesticide injection pipeline must contain a functional, automatic, quick-closing check valve to prevent the flow of fluid back toward the injection pump.

The pesticide injection pipeline must also contain a functional, normally closed, solenoid-operated valve located on the intake side of the injection pump and connected to the system interlock to prevent fluid from being withdrawn from the supply tank when the irrigation system is either automatically or manually shut down.

The system must contain functional interlocking controls to automatically shut off the pesticide injection pump when the water pump motor stops.

The irrigation line or water pump must include a functional pressure switch which will stop the water pump motor when the water pressure decreases to the point where pesticide distribution is adversely affected.

MALATHION 8 AQUAMUL
EPA REG. NO. 34704-474

Systems must use a metering pump such as a positive displacement injection pump (e.g., diaphragm pump) effectively designed and constructed of materials that are compatible with pesticides and capable of being fitted with a system interlock.

DIRECTIONS FOR DILUTION

DILUTE APPLICATION: Ground Application: Apply specified rate in 20 to 60 gallons of water per acre. Orchard Application: Apply specified rate in 100 to 800 gallons of water per acre.

CONCENTRATE APPLICATION: Ground Application: Apply specified rate in not less than 5 gallons of water per acre. Orchard Application: Apply specified rate in 20 to 100 gallons of water per acre. Special concentrate equipment is necessary for these uses.

AIR APPLICATION: Apply specified rate in 5 to 20 gallons of water per acre. Orchard rates should not be applied in less than 10 gallons of water per acre.

APPLICATIONS

Do not use this product for any uses other than those specified on this label. When using in the greenhouse or stored grain facilities as recommended on the label, use only with adequate ventilation. After application, ventilate thoroughly before occupying enclosed spaces. All rates are for a dilute spray. All rates are per acre.

ALFALFA, BIRDSFOOT TREFOIL, CLOVER, LESPEDEZA, LUPINE, VETCH: Aphid, armyworm, grasshoppers, clover leaf weevil, leafhopper, spider mites - 1¼ to 2 pts. Apply to alfalfa in bloom only in the evening or early morning when bees are not working in the fields or are not hanging on the outside of hives. Rates of 1¼ to 1½ pts. no time limitation. Rates over 1½ pts. to 2 pts., do not apply within 7 days of harvest.

ALFALFA, BIRDSFOOT TREFOIL, CLOVER, LESPEDEZA, LUPINE, VETCH (Seed Crops): Aphid, leafhoppers, lygus bugs - 1 to 1¼ pts. May be applied day of harvest. Apply to plants in bloom only in the evening or early morning when bees are not working in the fields or are not hanging on the outside of hives.

AMARANTH (Leafy Amaranth, Chinese Spinach, Tampala), ARRUGULA (Roquette), CELTRUCE, CHERVIL, CHRYSANTHEMUM (Edible-leafed, Garland), CORN SALAD, DOCK (Sorrel), FLORENCE FENNEL, ORACH, PARSLEY, PURSLANE (Garden and Winter): Aphid -1 to 2 pts. Do not apply within 7 days of harvest for all crops except parsley which is 21 days.

APRICOTS: Aphid, codling moth, orange tortrix, soft brown scale, terrapin scale - 4 to 10 pts. Do not apply within 7 days of harvest. Full coverage spray.

ASPARAGUS: Asparagus beetle, thrips - 1¼ pt. Do not apply within 1 day of harvest.

AVOCADOS: Green house thrips, Latania scale, omnivorous looper, soft brown scale, orange tortrix - 4 to 9 pts. Do not apply within 7 days of harvest.

BARLEY, OATS, RYE, WHEAT: Aphid, cereal leaf beetle, grasshoppers, greenbugs - 1¼ pt. Do not apply within 7 days of harvest.

BEANS (Dry & Succulent): Aphid, cucumber beetle, Japanese beetle, leafhopper, lygus bug, Mexican bean beetle, mites - 1¼ to 1¾ pt. Do not apply within 1 day of harvest. Do not graze or feed treated crop foliage to livestock.

BEETS (Garden & Table), DANDELIONS: Aphid - 1 to 2½ pts. Do not apply within 7 days of harvest.

MALATHION 8 AQUAMUL
EPA REG. NO. 34704-474

BLACKBERRIES, BOYSENBERRIES, DEWBERRIES, LOGANBERRIES, RASPBERRIES: Japanese beetle, leafhoppers, mites, thrips - 1 to 4 pts. Aphid, rose scale - 2 to 4 pts. Do not apply within 1 day of harvest.

BLUEBERRIES: Cherry fruit worm, cranberry fruit worm, Japanese beetle, plum curculio, sharp-nose leafhopper - 1½ to 2½ pts. Do not apply within 1 day of harvest.

BROCCOLI, BROCCOLI RAAB (Rapini), BRUSSELS SPROUTS, CABBAGE, CAULIFLOWER, CAVALO BROCCOLO, CHINESE BROCCOLI, CHINESE CABBAGE (Bok Choy, Napa), CHINESE MUSTARD CABBAGE, COLLARDS, KALE, KOHLRABI, MIZUNA, MUSTARD GREENS, MUSTARD SPINACH, RAPE GREENS, TURNIPS: Aphids, Cabbage looper, flea beetle, imported cabbageworm - 1½ to 2½. Do not apply with 7 days of harvest for all crops except broccoli which is 3 days.

CARROTS: Aphid - 1 to 2 pts. Leafhopper - 1½ to 2 pts. Do not apply within 7 days of harvest.

CELERY: Aphid, spider mites - 1 to 1½ pts. Do not apply within 7 days of harvest.

CHERRIES: Black cherry aphid, bud moth, cherry fruit fly, Forbes scale, fruit tree leaf roller, San Jose scale - 2½ to 8 pts. Lesser peach tree borer - 4 to 8 pts. Do not apply within 3 days of harvest. May injure foliage of some varieties.

CHESTNUTS: Mites - 2 to 5 pts. No time limitation.

CITRUS (Grapefruit, lemons, limes, oranges, tangerines (Mandarin or Mandarin Oranges, Tangors, and other hybrids of tangerines with other citrus) tangelos, kumquats): Aphid, black scale, California red scale, citricola scale, Florida red and purple scale, soft scale, thrips, yellow scale - 7 to 25 pts. Mediterranean fruit fly - 1 to 8 pts. Do not apply within 7 days of harvest. Do not apply during full bloom.

CORN: Aphid, cereal leaf beetle, corn earworm (apply to silks as soon as they appear. Make 3 to 4 applications at 2-3 day intervals as infestations warrant, reapply immediately after rain), corn rootworm-adult, grasshoppers, sap beetle, thrips - 1 pt. Do not apply within 5 days of harvest. For grain or forage use.

COTTON: Aphid, boll weevil, cotton leaf perforator, cotton leafworm, leafhoppers, lygus bug, mites, thrips, white flies, fall armyworm, fleahopper, garden webworm, grasshopper - 1½ to 4 pts. per acre. No time limitation.

CUCUMBERS, MELONS, PUMPKINS, SQUASH: Aphid, pickleworm, spider mites, thrips - 1 to 1¼ pts. Cucumber beetle - 1¼ pt. Do not apply within 3 days of harvest on pumpkins, 1 day of harvest on cucumbers, melons and squash. Do not apply unless plants are dry.

CURRENTS, GOOSEBERRIES: Mites, Japanese beetle - 1 to 2 pts. Currant aphid, imported currantworm - 2 pts. Do not apply within 3 days of harvest on Gooseberries, 1 day of harvest on currants.

EGGPLANT: Aphid, spider mite - ¾ to 3½ pts. Lace bug - 2 to 3½ pts. Do not apply within 3 days of harvest.

ENDIVE: Aphid, mites - 1 to 2 pts. Do not apply within 7 days of harvest.

MALATHION 8 AQUAMUL
EPA REG. NO. 34704-474

FIGS: Dried fruit beetle, vinegar flies - 2½ pts. plus 2 gals. unsulfurized molasses as a bait spray. Do not apply within 3 days of harvest.

FLAX: Grasshoppers -½ pt. Do not apply within 45 days of harvest.

GARLIC, LEEKS, SHALLOTS: Aphids, thrips -1 to 2 pts. Do not apply within 3 days of harvest of leeks and garlic, and 7 days of harvest of shallots.

GRAPES: Drosophila, Japanese beetle, leafhopper, mealybugs, spider mite, terrapin scale - 2 to 2 ¾ pts. Do not apply within 3 days of harvest. Caution - May cause injury to foliage on some varieties.

GRASS, GRASS HAY: Aphid, armyworm, grasshopper, leafhopper - 1¼ pt. No time limitation.

HOPS: Aphid - ½ to 1¼ pt. Do not apply within 7 days of harvest.

HORSERADISH, SALSIFY, SPINACH, SWISS CHARD, WATERCRESS: Aphid - 1 to 2 pts. Do not apply within 7 days of harvest.

LETTUCE: Aphid, leafhopper - 1¼ to 2 pts. Cabbage looper, mites - 2 pts. Do not apply within 14 days of harvest on leaf lettuce, 7 days of harvest on head lettuce.

MACADAMIA NUTS: Green stink bug - 3 to 15 pts. No time limitation.

MANGO, PASSION FRUIT, GUAVA: Fruit flies - ¾ pt. plus 1 lb. partially hydrolized yeast protein or enzymatic yeast hydrolyzate. Do not apply within 2 days of harvest.

OKRA: Aphid, Japanese beetle - 1½ pt. Do not apply within 1 day of harvest.

ONIONS (Bulb and Green) (Field or Greenhouse): Thrips - 1 to 2 pts. Onion maggot - 2 pts. Do not apply within 3 days of harvest.

PARSLEY, PARSNIPS, RADISHES, RUTABAGAS: Aphid - 1 to 2 pts. Do not apply within 21 days of harvest on parsley, 7 days of harvest on parsnips, radishes, 3 days of harvest on rutabagas.

PEACHES, NECTARINES: Aphid (green peach, black cherry, black peach, rusty plum), Japanese beetle, mites (European red, two-spotted) - 2½ to 9 pts. Cottony peach scale, lesser peach tree borer, plum curculio, oriental fruit moth, terrapin scale - 5 to 9 pts. Do not apply within 7 days of harvest. Full coverage spray.

PEACHES (Dormant and delayed dormant): Aphid, peach twig borer, scale (San Jose) - 4 to 9 pts. plus 6-8 gals. Super 94 440 Spray Oil. Use lower rate of Super 94 440 Spray Oil at delayed dormant and concentrate spray.

PEAS: Aphid, pea weevil - 1 to 2½ pt. Do not apply within 3 days of harvest. Do not graze or feed treated crop foliage to livestock.

PECANS: Aphid, mites, pecan bud moth, pecan leaf casebearer, pecan nut casebearer, pecan phylloxera - 2½ to 12½ pts. No time limitation.

PEPPERS: Aphid - ¾ to 1½ pts. Maggots - 1½ pts. Do not apply within 3 days of harvest.

MALATHION 8 AQUAMUL
EPA REG. NO. 34704-474

PEPPERMINT, SPEARMINT: Adult flea beetle, aphid, leafhoppers, spider mite - 1 pt. Do not apply within 7 days of harvest.

PINEAPPLE: Mealybug - 5 pts. Do not apply within 7 days of harvest.

POTATOES: Aphid, false chinch bug, leafhopper, mealybug - 1 to 3 pts. No time limitation.

RICE: Rice leaf miner, rice stink bug - 1½ pts. Do not apply within 7 days of harvest. Broadcast use only over intermittently flooded areas. Application may not made around bodies of water where fish or shellfish are grown and/or harvested commercially.

SORGHUM (Grain or Forage): Greenbugs -1 ½ pts. Do not apply within 7 days of harvest. Do not graze or feed forage to livestock.

STRAWBERRIES: Aphid, field crickets, lygus bugs, potato leafhopper, spider mite, spittlebug, strawberry leafroller, strawberry root weevil, thrips, white flies - 1 to 2 pts. Do not apply within 3 days of harvest.

SWEET CORN (Field or Greenhouse): Japanese beetle-1 pt. Do not apply within 5 days of harvest.

SWEET POTATOES: Leafhoppers - 1 to 1¾ pts. Morningglory leafminer - 1¾ pts. Do not apply within 3 days of harvest.

TOMATOES: Aphid, spider mite - 1 to 2 pts. Drosophila, tomato russet mite - 1½ to 3½ pts. army- worm, fruit worms - 3½ pts. Do not apply within 1 day of harvest at the 1 to 2 pt. rate. Rates over 2 pts. to 3½ pts. - do not apply within 5 days of harvest.

WALNUTS: Aphid, mites, walnut husky fly - 4 to 12½ pts. No time limitation.

ORNAMENTALS

Note: Before treating a large number of ornamental plants with MALATHION 8 AQUAMUL alone or as a tank mixture with any other material, make a test application on a few plants and observe 7-10 days prior to treating large areas to reduce the possibility of plant injury.

**MALATHION 8 AQUAMUL
EPA REG. NO. 34704-474**

CROP	REI (HRS)	RATE	PESTS	COMMENTS
FLOWERS, SHADE TREES And SHRUBS	12	1 pt. in 100 gals. of water as a dilute spray	Aphids, Euonymus Scale, European Pine Shoot Moth, Four-lined Leaf Bug, Japanese Beetle Adults, Lace Scale, Mealybugs, Millipedes, Oyster Shell Scale, Potato Leafhopper, Rose Leafhopper, Scurfy Scale, Spider Mites, Springtails, Sowbugs, Tarnished Plant Bug, Thrips, Whiteflies	CAUTION: Avoid use on certain ferns including Boston, Maidenhair and Pteris, as well as some species of Crassula and Canaetri Juniper. For Oyster shell, Fletch, Juniper, Oak kermes and Pine needle scales apply when scale crawlers have settled on foliage.
		1 ¼ pints in 100 gals. of water as a dilute spray	Azalea Scale, Bagworm, Birch Leafminer, Boxwood Leafminer, Fletch Scale, Florida-Red Scale, Juniper Scale, Magnolia Scale, Oak Kermes, Pine Leaf Scale, Tent Caterpillar	
		1 3/5 pts. in 100 gals. of water	Black Scale Crawler, Monterey Pine Scale	
		2 ½ pts in 100 gals. of water	Pine Needle Scale, Wax Scale	

SLASH PINE, PINE SEED ORCHARDS, AND CHRISTMAS TREE PLANTATIONS

CROP	REI (HRS)	RATE	PESTS	COMMENTS
SLASH PINE, PINE SEED ORCHARDS, And CHRISTMAS TREE PLANTATIONS	12	For ground application, mix 3/4 to 4/5 gals. of MALATHION 8 AQUAMUL in 100 gals. of water	Slash Pine Flower Thrips, European Pine Sawfly	Apply ¾ gals. of the mixture per tree on the smallest flowering trees. Mist blowers or airblast sprays may be used.
		For air application, mix 2/5 gals. of MALATHION 8 AQUAMUL in at least 5 gals. of water		Apply a minimum of 5 gals. of mixture per acre. Make two applications, the first when female flowers are in twig bud stage, the second one week prior to maximum flower receptivity to pollen.

MOSQUITO CONTROL

MOSQUITOES, FLIES, AND SMALL FLYING INSECTS: For use by trained personnel as a 2% to 5% Malathion fog, aerosol or space spray. To make a 2% solution dilute 1 part MALATHION 8 AQUAMUL in 45 parts water fuel oil or diesel oil. When using a kerosene-type solvent as a carrier, dilute 1 part MALATHION 8 AQUAMUL in 45 parts solvent consisting of 4 parts kerosene-type solvent and 1 part aromatic hydrocarbon-type solvent. Apply 0.58-2.86 gallons finished spray per acre. For a 5% solution, dilute 1 part MALATHION 8 AQUAMUL in 18 parts solvent. Apply 0.24-1.18 gallons finished spray per acre.

MOSQUITO LARVAE IN STANDING WATER

(Not registered for aquatic use in New York State.)

(Only for use in intermittently flooded areas, stagnant water, temporary rail ponds, and log ponds - KEEP OUT OF ANY FISH BEARING WATERS): Apply MALATHION 8 AQUAMUL at the rate of 8 fluid ounces per acre. Mix in sufficient water or oil to obtain even coverage when applied by air or ground equipment. Repeat applications as necessary. Avoid applying oil-based formulations to valuable ornamental plants as injury may occur. Broadcast use only over intermittently flooded areas. Application may not be made around bodies of water where fish or shell fish are grown and/or harvested commercially.

MALATHION 8 AQUAMUL
EPA REG. NO. 34704-474

SMALL GRAIN STORAGE FACILITIES

For a residual wall, floor, and machinery spray in grain elevators. In treating truck beds, box cars, and ships' holds before loading grain, apply 5 pts. per 25 gallons of water making thorough application. Before applying spray, clean elevators, box cars, etc. thoroughly. Remove and burn all sweepings and debris. Only corn, wheat, rye, oats and barley grain storage facilities may be treated.

**DROSOPHILA FLY AND DRIED FRUIT BEETLE CONTROL
ON OR AROUND CULL FRUIT AND VEGETABLE DUMPS**

Mix 7 ½ pints in 100 gallons of water. Apply as a drench, using 8 to 10 gallons of spray per 100 sq. ft. For best results, dumps should not be over 18 inches deep. Do not feed treated fruit and vegetables.

FLY CONTROL

STRAIGHT MALATHION SPRAYS			MALATHION BAIT SPRAYS		
AMOUNT OF SPRAY	AMOUNT MALATHION 8 AQUAMUL	AMOUNT OF BAIT SPRAY	AMOUNT MALATHION 8 AQUAMUL	SUGAR (or) UNSULFURIZED MOLASSES/CORN SYRUP	
2½ gals.	¾ cup	2½ gals.	¾ cup	1 cup	1 cup
12 gals.	1¼ pts.	12 gals.	1¼ pts.	2½ lbs.	1 qt.
100 gals.	1¼ gals.	100 gals.	1¼ gals.	20 lbs.	2 gals.

STORAGE AND DISPOSAL

Do not contaminate water, food, or feed by storage or disposal.

PESTICIDE STORAGE: Store in cool, dry, well-ventilated area. Store separately from strong alkalis and strong oxidizers. Keep container tightly closed when not in use.

PESTICIDE DISPOSAL: Pesticide wastes are toxic. Improper disposal of excess pesticide, spray mixture, or rinsate is a violation of Federal law. If these wastes cannot be disposed of by use according to label instructions, contact your State Pesticide or Environmental Control Agency, or the Hazardous Waste representative at the nearest EPA Regional Office for guidance.

CONTAINER DISPOSAL: Nonrefillable container. Do not reuse this container to hold materials other than pesticides or dilute pesticides (rinsate). After emptying and cleaning, it may be allowable to temporarily hold rinsate or other pesticide-related materials in the container. Contact your state regulatory agency to determine allowable practices in your state. Once cleaned, some agricultural plastic pesticide containers can be taken to a container collection site or picked up for recycling. To find the nearest site, contact your chemical dealer or manufacturer, or contact The Agricultural Container Recycling Council (ACRC) at www.acrecycle.org. If not recycled, then puncture and dispose of in a sanitary landfill, or incineration, or if allowed by state and local authorities, by burning. If burned, stay out of smoke.

Triple rinse or pressure rinse container (or equivalent) promptly after emptying.

For packages up to 5 gallons: Triple rinse as follows: Empty the remaining contents into application equipment or a mix tank and drain for 10 seconds after the flow begins to drip. Fill the container ¼ full with water and recap. Shake for 10 seconds. Pour rinsate into application equipment or a mix tank or store rinsate for later use or disposal. Drain for 10 seconds after the flow begins to drip. Repeat this procedure two more times. **Pressure rinse as follows:** Empty the remaining contents into application equipment or a mix tank and continue to drain for 10 seconds after the flow begins to drip. Hold container upside down over application equipment or mix tank or collect rinsate for later use or disposal. Insert pressure rinsing nozzle in the side of the container, and rinse at about 40 PSI for at least 30 seconds. Drain for 10 seconds after the flow begins to drip.

For packages greater than 5 gallons or 50 pounds: Triple rinse as follows: Empty the remaining contents into application equipment or a mix tank. Fill the container ¼ full with water. Replace and tighten closures. Tip container on its side and roll it back and forth, ensuring at least one complete revolution, for 30 seconds. Stand the container on its end and tip it back and forth several times. Turn the container over onto its other end and tip it back and forth several times.

MALATHION 8 AQUAMUL
EPA REG. NO. 34704-474

Storage & Disposal cont'd.:

Empty the rinsate into application equipment or a mix tank or store rinsate for later use or disposal. Repeat this procedure two more times. **Pressure rinse as follows:** Empty the remaining contents into application equipment or a mix tank and continue to drain for 10 seconds after the flow begins to drip. Hold container upside down over application equipment or mix tank or collect rinsate for later use or disposal. Insert pressure rinsing nozzle in the side of the container, and rinse at about 40 PSI for at least 30 seconds. Drain for 10 seconds after the flow begins to drip. **For refillable containers:** Refill this container with pesticide only. Do not reuse this container for any other purpose. Cleaning the container before final disposal is the responsibility of the person disposing of the container. Cleaning before refilling is the responsibility of the refiller. To clean the container before final disposal, empty the remaining contents from this container into application equipment or mix tank. Fill the container about 10 percent full with water. Agitate vigorously or recirculate water with the pump for 2 minutes. Pour or pump rinsate into application equipment or rinsate collection system. Repeat this rinsing procedure two more times.

For help with any spill, leak, fire or exposure involving this material, call day or night CHEMTREC – 1-800-424-9300.

CONDITIONS OF SALE AND LIMITATION OF WARRANTY AND LIABILITY

BEFORE BUYING OR USING THIS PRODUCT, read the entire Directions for Use and the following Conditions of Sale and Limitation of Warranty and Liability. By buying or using this product, the buyer or user accepts the following Conditions of Sale and Limitation of Warranty and Liability, which no employee or agent of LOVELAND PRODUCTS, INC. or the seller is authorized to vary in any way.

Follow the Directions for Use of this product carefully. It is impossible to eliminate all risks inherently associated with the use of this product. Crop or other plant injury, ineffectiveness, or other unintended consequences may result from such risks as weather or crop conditions, mixture with other chemicals not specifically identified in this product's label, or use of this product contrary to the label instructions, all of which are beyond the control of LOVELAND PRODUCTS, INC. and the seller. The buyer or user of this product assumes all such inherent risks.

Subject to the foregoing inherent risks, LOVELAND PRODUCTS, INC. warrants that this product conforms to the chemical description on the label and is reasonably fit for the purposes stated in the Directions for Use when the product is used in strict accordance with such Directions for Use under normal conditions of use. EXCEPT AS WARRANTED IN THIS LABEL AND TO THE EXTENT CONSISTENT WITH APPLICABLE LAW, THIS PRODUCT IS SOLD "AS IS," AND LOVELAND PRODUCTS, INC. MAKES NO OTHER WARRANTY, EXPRESS OR IMPLIED, INCLUDING BUT NOT LIMITED TO MERCHANTABILITY, FITNESS FOR A PARTICULAR PURPOSE, OR ELIGIBILITY OF THIS PRODUCT FOR ANY PARTICULAR TRADE USAGE.

IN THE UNLIKELY EVENT THAT BUYER OR USER BELIEVES THAT LOVELAND PRODUCTS, INC. HAS BREACHED A WARRANTY CONTAINED IN THIS LABEL AND TO THE EXTENT REQUIRED BY APPLICABLE LAW, BUYER OR USER MUST SEND WRITTEN NOTICE OF ITS CLAIM TO THE FOLLOWING ADDRESS: LOVELAND PRODUCTS, INC., ATTENTION: LAW DEPARTMENT, P.O. BOX 1286, GREELEY, CO 80632-1286.

TO THE EXTENT CONSISTENT WITH APPLICABLE LAW, THE BUYER'S OR USER'S EXCLUSIVE REMEDY FOR ANY INJURY, LOSS, OR DAMAGE RESULTING FROM THE HANDLING OR USE OF THIS PRODUCT, INCLUDING BUT NOT LIMITED TO CLAIMS OF BREACH OF WARRANTY OR CONTRACT, NEGLIGENCE, STRICT LIABILITY, OR OTHER TORTS, SHALL BE LIMITED TO ONE OF THE FOLLOWING, AT THE ELECTION OF LOVELAND PRODUCTS, INC. OR

**MALATHION 8 AQUAMUL
EPA REG. NO. 34704-474**

THE SELLER: DIRECT DAMAGES NOT EXCEEDING THE PURCHASE PRICE OF THE PRODUCT OR REPLACEMENT OF THE PRODUCT. TO THE EXTENT CONSISTENT WITH APPLICABLE LAW, LOVELAND PRODUCTS, INC. AND THE SELLER SHALL NOT BE LIABLE TO THE BUYER OR USER OF THIS PRODUCT FOR ANY CONSEQUENTIAL, SPECIAL, OR INDIRECT DAMAGES, OR DAMAGES IN THE NATURE OF A PENALTY.

FORMULATED FOR



P.O. BOX 1286, GREELEY, COLORADO 80632-1286

13

Appendix 7: Malathion 8 Aquamul® MSDS

MATERIAL SAFETY DATA SHEET

MALATHION 8 AQUAMUL

FOR CHEMICAL EMERGENCY, SPILL, LEAK, FIRE, EXPOSURE OR ACCIDENT, CALL CHEMTREC - DAY OR NIGHT 1-800-424-9300

1. CHEMICAL PRODUCT AND COMPANY IDENTIFICATION

FORMULATED FOR:

LOVELAND PRODUCTS, INC.
P.O. Box 1286 • Greeley, CO 80632-1286

24-Hour Emergency Phone: 1-800-424-9300

Medical Emergencies: 1-866-944-8565

U.S. Coast Guard National Response Center: 1-800-424-8802

PRODUCT NAME: MALATHION 8 AQUAMUL

CHEMICAL NAME: Malathion; (O-O-Dimethyl phosphorodithioate of diethyl mercaptosuccinate)

CHEMICAL FAMILY: Organophosphate Insecticide

EPA REG. NO.: 34704-474

MSDS Number: 000474-11-LPI

MSDS Revisions: Sections 7, 8, 12, and 13

Date of Issue: 05/23/11

Supersedes: 08/27/09

2. HAZARDS IDENTIFICATION SUMMARY

KEEP OUT OF REACH OF CHILDREN – CAUTION – Harmful if swallowed or absorbed through skin. Causes moderate eye irritation. Avoid contact with skin, eyes, or clothing. Prolonged or frequently repeated skin contact may cause allergic reaction in some individuals.

This product is straw to amber colored liquid with a mild petroleum odor. Primary routes of entry are Inhalation, eye contact and skin contact.

Warning Statements:

NOTE TO PHYSICIAN: This product is an organophosphate (cholinesterase-inhibiting) insecticide and may cause cholinesterase inhibition. Atropine is antidotal and should be given in multiple doses as necessary until the patient is atropinized. 2-PAM may be effective as an adjunct to atropine. Monitor serum and RBC cholinesterase. Administer intravenous fluids cautiously, if needed, to correct dehydration. Symptoms of cholinesterase inhibition include salivation, gastrointestinal hypermotility, abdominal cramping, nausea, diarrhea, sweating, miosis, tearing, blurred vision, headache, dizziness, ataxia, bradycardia, dyspnea, cyanosis, and muscle twitching or tremors. In extreme cases, tetany, mental confusion, incontinence, weakness, collapse, paralysis, convulsive seizures, and even death, can occur.

3. COMPOSITION, INFORMATION ON INGREDIENTS

<u>Chemical Ingredients:</u>	<u>Percentage by Weight:</u>	<u>CAS No.</u>	<u>TLV (Units)</u>
Malathion	81.80	121-75-5	15 mg/m ³ (Skin)
Inert Ingredients	18.20		

4. FIRST AID MEASURES

If swallowed: Call a poison control center or doctor immediately for treatment advice. Have person sip a glass of water if able to swallow. Do not induce vomiting unless told to do so by a poison control center or doctor. Do not give anything by mouth to an unconscious person.

If inhaled: Move person to fresh air. If person is not breathing, call 911 or an ambulance, then give artificial respiration, preferably mouth-to-mouth if possible. Call a poison control center or doctor for further treatment advice.

If on skin or clothing: Take off contaminated clothing. Rinse skin immediately with plenty of water for 15-20 minutes. Call a poison control center or doctor for treatment advice.

If in eyes: Hold eye open and rinse slowly and gently with water 15-20 minutes. Remove contact lenses, if present, after the first 5 minutes, then continue rinsing eye. Call a poison control center or doctor for treatment advice.

FOR A MEDICAL EMERGENCY INVOLVING THIS PRODUCT CALL: 1-866-944-8565. Have the product label or container with you when calling a poison control center or doctor, or going for treatment.

5. FIRE FIGHTING MEASURES

FLASH POINT (°F/Test Method): 175°F / 79.4°C (TCC)

FLAMMABLE LIMITS (LFL & UFL): None established

EXTINGUISHING MEDIA: Dry chemical, carbon dioxide, foam, water spray or fog.

HAZARDOUS COMBUSTION PRODUCTS: Thermal decomposition products include oxides of sulfur and phosphorus-containing compounds.

SPECIAL FIRE FIGHTING PROCEDURES: Wear self-contained breathing apparatus with full protective clothing. Fight fire from upwind and keep all non-essential personnel out of area.

UNUSUAL FIRE AND EXPLOSION HAZARDS: None known.

6. ACCIDENTAL RELEASE MEASURES

STEPS TO BE TAKEN IF MATERIAL IS RELEASED OR SPILLED:

For small spills, absorb with an absorbent material such as pet litter. Sweep up and transfer to containers for possible land application according to label use or for proper disposal. Check local, state and federal regulations for proper disposal. Flush the area with water to remove any residue.

CAUTION: Keep spills and cleaning runoff out of municipal sewers and open bodies of water.

7. HANDLING AND STORAGE

HANDLING: 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 after handling this product. Wash the outside of gloves before removing. As soon as possible, wash thoroughly and change into clean clothing.

MATERIAL SAFETY DATA SHEET

MALATHION 8 AQUAMUL

STORAGE: Malathion 8 Aquamul should be stored in the original unopened container in a secure, dry place. Do not contaminate with other pesticides or fertilizers. The product should never be heated above 55 °C (131 °F), and should not be stored for long periods of time at a temperature in excess of 25 °C (77 °F). Store in a cool, dry, well-ventilated area. Store separately from strong alkalies and strong oxidizers. Keep container tightly closed when not in use. Do not contaminate water, food, or feed by storage or disposal.

Personal Protective Equipment (PPE): For all formulations and all use patterns – mixers, loaders, applicators, flaggers, and other handlers must wear: long sleeved shirt and long pants, shoes plus socks, and chemical-resistant gloves. Some materials that are chemical-resistant to this product are barrier laminate, butyl rubber, nitrile rubber or Viton®. If you want more options, follow the instructions for Category (F) on an EPA chemical resistance category selection chart. Follow manufacturer's instructions for cleaning and maintaining PPE. If no instructions for washables, use detergent and hot water. Keep and wash PPE separately from other laundry. Discard clothing and other absorbent materials that have been drenched or heavily contaminated with this product's concentrate. Do not reuse them.

8. EXPOSURE CONTROLS / PERSONAL PROTECTION

ENGINEERING CONTROLS: Pilots must use an enclosed cockpit in a manner that is consistent with the WPS for agricultural pesticides [40 CFR 170.240(d)(6)]. Pilots must wear the PPE required on product labeling for applicators.

RESPIRATORY PROTECTION: Not normally required, if vapors or mists exceed acceptable levels, wear a NIOSH approved pesticide respirator.

EYE PROTECTION: Chemical goggles or shielded safety glasses.

SKIN PROTECTION: Wear protective clothing: long-sleeved shirts and pants, shoes with socks. Wear chemical-resistant gloves.

Malathion	OSHA PEL 8 hr TWA 15 mg/m ³ (Skin)	ACGIH TLV-TWA 1 mg/m ³ (Inhalable fraction and vapor)
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9. PHYSICAL AND CHEMICAL PROPERTIES

APPEARANCE AND ODOR: Straw to amber liquid with mild petroleum odor.

SOLUBILITY: Soluble

SPECIFIC GRAVITY (Water = 1): 1.1934 g/ml

BULK DENSITY: 9.96 lbs/gal.

VAPOR PRESSURE: Not established

BOILING POINT: Not established

PERCENT VOLATILE (by volume): Not established

EVAPORATION RATE: Not established

Note: These physical data are typical values based on material tested but may vary from sample to sample. Typical values should not be construed as a guaranteed analysis of any specific lot or as specification items.

10. STABILITY AND REACTIVITY

STABILITY: Stable

CONDITIONS TO AVOID: Excessive heat, open flame or extreme cold.

INCOMPATIBILITY: Strong bases, acids, and oxidizers.

HAZARDOUS DECOMPOSITION PRODUCTS: Thermal decomposition – oxides of sulfur and phosphorus-containing compounds.

HAZARDOUS POLYMERIZATION: Will not occur.

11. TOXICOLOGICAL INFORMATION

Acute Oral LD₅₀ (rat): 550 mg/kg (Technical)	Acute Dermal LD₅₀ (rabbit): > 2000 mg/kg (Technical)
Eye Irritation (rabbit): Slight irritation (Technical)	Skin Irritation (rabbit): Slight irritation (Technical)
Inhalation LC₅₀ (rat): >5.2 mg/L (4 hr) (Technical).	Skin Sensitization (Guinea Pig): Not a sensitizer (Technical).
Carcinogenic Potential: None listed in OSHA, NTP, IARC or ACGIH	

12. ECOLOGICAL INFORMATION

Malathion is toxic to aquatic organisms, including fish and invertebrates. This product may contaminate water through drift of spray in wind. This product has a high potential for runoff after application. Use care when applying in or to an area which is adjacent to any body of water, and do not apply when weather conditions favor drift from target area. Poorly draining soils and soils with shallow water tables are more prone to produce runoff that contains this product. A level, well maintained vegetative buffer strip between areas to which this product is applied and surface water features such as ponds, streams, and springs will reduce the potential for contamination of water from rainfall runoff. Runoff of this product will be reduced by avoiding applications when rainfall is forecasted to occur within 48 hours. Do not apply directly to water, or to areas where surface water is present or to intertidal areas below the mean high water mark. Do not contaminate water when disposing of equipment washwater or rinsate. To protect the environment, do not allow pesticide to enter or run off into storm drains, drainage ditches, gutters or surface waters. This pesticide is highly toxic to bees exposed to direct treatment on blooming crops or weeds. Do not apply this product or allow it to drift to blooming crops or weeds while bees are actively visiting the treatment area. For commercial, industrial, and institutional use products packaged in containers equal or greater than 5 gallons or 50 pounds: Do not discharge effluent containing this product into lakes, streams, ponds, estuaries, oceans, or other waters unless in accordance with the requirements of a National Pollutant Discharge Elimination System (NPDES) permit and the permitting authority has been notified in writing prior to discharge. Do not discharge effluent containing this product to sewer systems without previously notifying the local sewage treatment plant authority. For guidance contact your State Water Board or Regional Office of the EPA.

13. DISPOSAL CONSIDERATIONS

PESTICIDE DISPOSAL: To avoid wastes, use all material in this container by application according to label directions. If wastes cannot be avoided, offer remaining product to a waste disposal facility or pesticide disposal program (often such programs are run by state or local governments or by industry).

CONTAINER DISPOSAL: Nonrefillable container. Do not reuse or refill this container. Offer for recycling, if available. Triple rinse container (or equivalent) promptly after emptying. For containers up to 5 gallons: Triple rinse as follows: Empty the remaining contents into application equipment or a mix tank and drain for 10 seconds after the flow begins to drip. Fill the container ¼ full with water and recap. Shake for 10 seconds. Pour rinsate into application equipment or a mix tank or store rinsate for later use or disposal. Drain for 10 seconds after the flow begins to drip. Repeat this procedure two more times. For containers greater than 5 gallons or 50 pounds: Triple rinse as follows: Empty the remaining contents into application equipment or a mix tank. Fill the container ¼ full with water. Replace and tighten closures. Tip container on its side and roll it back and forth, ensuring at least one complete revolution, for 30 seconds. Stand the container on its end and tip it back and forth several times. Turn the container over onto its other end and tip it back and forth several times. Empty the rinsate into application equipment or a mix tank or store rinsate for later use or disposal. Repeat this procedure two more times. If not recycled, then puncture and dispose of in a sanitary landfill. Triple rinse or pressure rinse container (or equivalent) promptly after emptying. For refillable containers: Refill this container with pesticide only. Do not reuse this container for any other purpose. Cleaning the container before final disposal is the responsibility of the person disposing of the container. Cleaning before refilling is the responsibility of the refiller.

MATERIAL SAFETY DATA SHEET

MALATHION 8 AQUAMUL

To clean the container before final disposal, empty the remaining contents from this container into application equipment or mix tank. Fill the container about 10 percent full with water. Agitate vigorously or recirculate water with the pump for 2 minutes. Pour or pump rinsate into application equipment or rinsate collection system. Repeat this rinsing procedure two more times.

14. TRANSPORT INFORMATION

DOT Shipping Description: LESS THAN 12.5 GALLONS NOT REGULATED BY USDOT.

DOT Shipping Description: ENVIRONMENTALLY HAZARDOUS SUBSTANCE, LIQUID, N.O.S., 9, UN3082, III (MALATHION) RQ ERG GUIDE 171

U.S. Surface Freight Classification: INSECTICIDES, INSECT REPELLENTS, NOI, OTHER THAN POISON (NMFC 102120, CLASS: 60)

Consult appropriate ICAO/IATA and IMDG regulations for shipment requirements in the Air and Maritime shipping modes.

15. REGULATORY INFORMATION

NFPA & HMIS Hazard Ratings:

NFPA

2	Health	0	Least
2	Flammability	1	Slight
0	Instability	2	Moderate
		3	High
		4	Severe

HMIS

2	Health
2	Flammability
0	Reactivity
H	PPE

SARA Hazard Notification/Reporting

SARA Title III Hazard Category:

Immediate	<u>Y</u>
Delayed	<u>Y</u>

Fire	<u>N</u>
Reactive	<u>N</u>

Sudden Release of Pressure	<u>N</u>
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Reportable Quantity (RQ) under U.S. CERCLA: Malathion (CAS: 121-75-5): 100 pounds

SARA, Title III, Section 313: Malathion (CAS: 121-75-5) 81.8%

RCRA Waste Code: Not listed

CA Proposition 65: Not listed.

16. OTHER INFORMATION

MSDS STATUS: Sections 7, 8, 12, and 13 revised

PREPARED BY: Registrations and Regulatory Affairs

REVIEWED BY: Environmental/ Regulatory Services

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Disclaimer and Limitation of Liability: This data sheet was developed from information on the constituent materials identified herein and does not relate to the use of such materials in combination with any other material or process. No warranty is expressed or implied with respect to the completeness or ongoing accuracy of the information contained in this data sheet, and LOVELAND PRODUCTS, Inc. disclaims all liability for reliance on such information. This data sheet is not a guarantee of safety. Users are responsible for ensuring that they have all current information necessary to safely use the product described by this data sheet for their specific purpose.

Appendix 8: Activator 90® Label

ACTIVATOR 90

**NON-IONIC SURFACTANT
PENETRANT • ANTIFOAMING AGENT**

Principal Functioning Agents:

Alkylphenol ethoxylate, alcohol ethoxylate and tall oil fatty acid	90%
Constituents ineffective as spray adjuvant.....	10%
TOTAL	100%

CA Reg. No. 34704-50034
WA Reg. No. 34704-04001

**KEEP OUT OF REACH OF CHILDREN
CAUTION**

NET CONTENTS:

- ☐ 30 GL (113.6 L)
☐ 275 GL (1040.9 L)
☐ _____



Loveland Products, Inc. • PO Box 1286 • Greeley, CO 80632-1286

CAUTION: Harmful if swallowed, absorbed through skin or inhaled. Avoid breathing vapor or spray mist. Remove contaminated clothing and wash clothing before reuse. Causes moderate eye irritation. Avoid contact with eyes, skin or clothing. Wash thoroughly with soap and water after handling.

Personal Protective Equipment: Wear Long-sleeved shirt and long pants. Socks, Shoes and Gloves.

First Aid:

If on skin or clothing: Take off contaminated clothing. Rinse skin immediately with plenty of water for 15-20 minutes. **If in eyes:** Hold eye open and rinse slowly and gently with water for 15 to 20 minutes. Remove contact lenses, if present, after the first 5 minutes, then continue rinsing eye. **If swallowed:** Call a poison control center or doctor immediately for treatment advice. Have the person sip a glass of water if able to swallow. Do not induce vomiting unless told to do so by the poison control center or doctor. Do not give anything by mouth to an unconscious person. **If inhaled:** Move person to fresh air. If person is not breathing, call 911 or an ambulance, then give artificial respiration, preferably by mouth-to-mouth, if possible.

FOR A MEDICAL EMERGENCY INVOLVING THIS PRODUCT, CALL 1-866-944-8565.

General: **ACTIVATOR 90** is a low-foaming, non-ionic type spreader adjuvant. **ACTIVATOR 90** provides quick wetting, more uniform distribution, and increases retention of spray by reducing surface tension of the spray droplets. **ACTIVATOR 90** is a water soluble adjuvant that may also

be used as an interfacing agent for wettable powders. Variations in conditions of use can cause some variation in the amount of **ACTIVATOR 90** required. The minimum required to give a smooth, uniform coverage usually gives the most effective results.

Mixing Instructions: For wettable powders and water soluble materials, add **ACTIVATOR 90** in water before adding pesticide to spray tank. For emulsifiable products, add **ACTIVATOR 90** after a good emulsion is formed.

Directions for Use: Some pesticides have stated adjuvant use rates. In all cases, the pesticide manufacturer's label should be consulted regarding specific adjuvant use recommendations and that rate followed. Do not add adjuvant at a level that would exceed 5% of the finished spray volume. For tank mix compatibility concerns, conduct a jar test of the proposed mixture to ensure compatibility of all components. Mix components in the same ratio as the proposed tank mix. Not for aquatic use in Washington.

Herbicides, Defoliants, Desiccants:

1 to 4 pints/100 gallons of spray mixture.

Insecticides, Fungicides, Acaracides, Plant Growth Regulators, Foliar Nutrients:

1 to 4 pints/100 gallons of spray mixture.

Turf, Ornamental, and Industrial Spraying: 1 to 3 ounces per 5 gallons of spray mixture. **NOTE:** This product has demonstrated excellent plant safety; however, not all species and varieties have been tested. Before treating a large area, treat a small area and observe prior to full-scale application.

DO NOT USE ON ROSES.

Storage: Store in cool, dry place. Store in original container. Keep container tightly closed. Do not reuse empty container. **Disposal:** Do not contaminate water, food, or feed by storage or disposal. Wastes may be disposed of on-site or at an approved waste disposal facility. Triple rinse (or equivalent) adding rinse water to spray tank. Offer container for recycling or dispose of container in sanitary landfill, or by other procedures approved by appropriate authorities. Recycling decontaminated containers is the best option of container disposal. The Agricultural Container Recycling Council (ACRC) operates the national recycling program. To contact your state and local ACRC recycler visit the ACRC web page at www.acrecycle.org.

For help with any spill, leak, fire or exposure involving this material, call day or night CHEMTREC 1-800-424-9300.

CONDITIONS OF SALE AND LIMITATION OF WARRANTY AND LIABILITY BEFORE

BUYING OR USING THIS PRODUCT, read the Directions for Use and the following Conditions of Sale and Limitation of Warranty and Liability. By buying or using this product, the buyer or user accepts the following Conditions of Sale and Limitation of Warranty and Liability, which no employee or agent of LOVELAND PRODUCTS, INC. or the seller is authorized to vary. LOVELAND PRODUCTS, INC. warrants that this product conforms to the chemical description on the label and is reasonably fit for the purposes stated in the Directions for Use, when the product is used in accordance with such Directions for Use under normal conditions of use. LOVELAND PRODUCTS, INC. MAKES NO OTHER WARRANTY, EXPRESS OR IMPLIED, INCLUDING BUT NOT LIMITED TO MERCHANTABILITY OR FITNESS FOR A PARTICULAR PURPOSE. THE BUYER'S OR USER'S EXCLUSIVE REMEDY FOR ANY INJURY, LOSS, OR DAMAGE RESULTING FROM THE HANDLING OR USE OF THIS PRODUCT SHALL BE LIMITED TO ONE OF THE FOLLOWING, AT THE ELECTION OF LOVELAND PRODUCTS, INC. OR THE SELLER: DIRECT DAMAGES NOT EXCEEDING THE PURCHASE PRICE OF THE PRODUCT OR REPLACEMENT OF THE PRODUCT. LOVELAND PRODUCTS, INC. AND THE SELLER SHALL NOT BE LIABLE TO THE BUYER OR USER OF THIS PRODUCT FOR ANY CONSEQUENTIAL, SPECIAL, OR INDIRECT DAMAGES, OR DAMAGES IN THE NATURE OF A PENALTY.

Appendix 9: Activator 90® MSDS

MATERIAL SAFETY DATA SHEET

ACTIVATOR 90

FOR CHEMICAL EMERGENCY, SPILL, LEAK, FIRE, EXPOSURE OR ACCIDENT, CALL CHEMTREC - DAY OR NIGHT 1-800-424-9300

1. CHEMICAL PRODUCT AND COMPANY IDENTIFICATION

FORMULATED FOR:

LOVELAND PRODUCTS, INC.
P.O. Box 1286 • Greeley, CO 80632-1286

24-Hour Emergency Phone: 1-800-424-9300
Medical Emergencies: 1-866-944-8565
U.S. Coast Guard National Response Center: 1-800-424-8802

PRODUCT NAME: ACTIVATOR 90
CHEMICAL NAME: Mixture of Alkyl Polyoxyethylene Ether, free fatty acids and water
CHEMICAL FAMILY: Surfactant
CA REG. NO.: 34704-50034
WA REG. NO.: 34704-04001
MSDS Number: 8000586-10-LPI

MSDS Revisions: Sections 1 and 4

Date Of Issue: 07/07/10

Supersedes: 10/06/08

2. HAZARDS IDENTIFICATION SUMMARY

KEEP OUT OF REACH OF CHILDREN - CAUTION – Harmful if swallowed, absorbed through skin, or inhaled. Avoid breathing vapor or spray mist. Remove contaminated clothing and wash clothing before reuse. Causes moderate eye irritation. Avoid contact with eyes, skin, or clothing. Wash thoroughly with soap and water after handling.

This product is an amber colored liquid with a fatty odor.

3. COMPOSITION, INFORMATION ON INGREDIENTS

<u>Chemical Ingredients:</u>	<u>Percentage by Weight:</u>	<u>CAS No.</u>	<u>TLV (Units)</u>
Alkyl Polyoxyethylene ether and free fatty acids	90.00	Mixture	none established
Other Ingredients	10.00		

4. FIRST AID MEASURES

If on Skin or clothing: Take off contaminated clothing. Rinse skin immediately with plenty of water for 15 – 20 minutes.
If in Eyes: Hold eye open and rinse slowly and gently with water for 15 – 20 minutes. Remove contact lenses, if present, after the first 5 minutes, then continue rinsing eye.
If Swallowed: Call a poison control center or doctor immediately for treatment advice. Have the person sip a glass of water if able to swallow. Do not induce vomiting unless told to do so by the poison control center or doctor. Do not give anything by mouth to an unconscious person.
If Inhaled: Move person to fresh air. If person is not breathing, call 911 or an ambulance, then give artificial respiration by mouth-to-mouth, if possible.

FOR A MEDICAL EMERGENCY INVOLVING THIS PRODUCT CALL: 1-866-944-8565.

5. FIRE FIGHTING MEASURES

FLASH POINT (°F/Test Method): >230°F / >110°C
FLAMMABLE LIMITS (LFL & UFL): Not established
EXTINGUISHING MEDIA: Water fog, alcohol foam, dry chemical or carbon dioxide (CO₂) to extinguish flames.
HAZARDOUS COMBUSTION PRODUCTS: None known.
SPECIAL FIRE FIGHTING PROCEDURES: Use water spray to cool containers exposed to fire. Spilled material creates extremely slippery conditions, use caution. Wear self-contained breathing apparatus and full protective gear.
UNUSUAL FIRE AND EXPLOSION HAZARDS: Petroleum hydrocarbon component is combustible. Vapors or fumes will ignite and flashback.

6. ACCIDENTAL RELEASE MEASURES

STEPS TO BE TAKEN IF MATERIAL IS RELEASED OR SPILLED:

Wear appropriate personal protective equipment (refer to Section 8) when responding to spills. Shut off source of leak if safe to do so. Dike and contain spill. Soak up residue with absorbent such as clay, sand or other suitable material and dispose of properly. Flush area with water to remove trace residue. Contain runoff from residue flush and dispose of properly. Place in container for proper disposal. Check local, state and federal regulations for proper disposal.

CAUTION: Keep spills and cleaning runoff out of municipal sewers and open bodies of water.

7. HANDLING AND STORAGE

HANDLING: Wear impervious gloves when handling. Keep away from heat, sparks, and flames while in use. Wash with soap and water before eating, drinking, smoking, applying cosmetics, or using toilet facilities. Keep away from children, feed and foodstuffs, fertilizers and seed.
STORAGE: Store in a cool, dry place. Store in original container. Keep container tightly closed. Do not reuse empty container. Do not contaminate water, food or feed by storage or disposal.

MATERIAL SAFETY DATA SHEET

ACTIVATOR 90

8. EXPOSURE CONTROLS / PERSONAL PROTECTION

ENGINEERING CONTROLS: Not required.
RESPIRATORY PROTECTION: Wear a NIOSH approved respirator if necessary.
EYE PROTECTION: Chemical goggles or shielded safety glasses.
SKIN PROTECTION: Wear protective clothing. Wear impervious rubber or chemical-resistant gloves.

	OSHA PEL 8 hr TWA	ACGIH TLV-TWA
For product	not established	not established

9. PHYSICAL AND CHEMICAL PROPERTIES

APPEARANCE AND ODOR: Amber colored liquid with a fatty odor	BULK DENSITY: 8.35 lbs/gal.	SOLUBILITY: Soluble
SPECIFIC GRAVITY (Water = 1): 1.001 g/ml	BOILING POINT: 101.2°C/215°F	pH: 6.0 (neat)
VAPOR PRESSURE: Not established	EVAPORATION RATE: Not established	
PERCENT VOLATILE (by volume): 65.0%		

Note: These physical data are typical values based on material tested but may vary from sample to sample.
 Typical values should not be construed as a guaranteed analysis of any specific lot or as specification items.

10. STABILITY AND REACTIVITY

STABILITY: Stable
CONDITIONS TO AVOID: None known.
INCOMPATIBILITY: Avoid contact with strong oxidizers, strong acids and bases at high temperatures.
HAZARDOUS DECOMPOSITION PRODUCTS: Carbon Monoxide from burning.
HAZARDOUS POLYMERIZATION: Will not occur.

11. TOXICOLOGICAL INFORMATION

Acute Oral LD₅₀ (rat): 3870-5000 mg/kg	Acute Dermal LD₅₀ (rabbit): >2000 mg/kg
Eye Irritation (rabbit): Mild to moderate irritant	Skin Irritation (rabbit): Minor irritant
Inhalation LC₅₀ (rat): 1.42 mg/L (4 HR)	Skin Sensitization (guinea pig): Not a sensitizer.
Carcinogenic Potential: None listed by OSHA, NTP, IARC, and ACGIH as a carcinogen	

12. ECOLOGICAL INFORMATION

Aquatic Acute Toxicity:

Guppy: 96 HR LC₅₀ 12.7 mg/L – 96 HR No Effect: 5.8 mg/L – **Daphnia Magna:** 24 HR EC₅₀ 5.2 mg/L – 24 HR No Effect 1 mg/L.

13. DISPOSAL CONSIDERATIONS

Triple rinse (or equivalent), adding rinse water to spray tank. Offer container for recycling or dispose of in a sanitary landfill or by other procedures approved by state and local authorities. Recycling decontaminated containers is the best option of container disposal. The Agricultural Container Recycling Council (ACRC) operates the national recycling program. To contact your state and local ACRC recycler visit the ACRC web page at <http://www.acrecycle.org/>. Wastes may be disposed of on site or at an approved waste disposal facility. Do not contaminate water, food or feed by storage or disposal.

14. TRANSPORT INFORMATION

DOT Shipping Description: NOT REGULATED BY USDOT.
Freight Classification: ADHESIVES, ADJUVANTS, SPREADERS OR STICKERS (NMFC 4610: CLASS: LTL 60, TL 35)
 Consult appropriate ICAO/IATA and IMDG regulations for shipment requirements in the Air and Maritime shipping modes.

15. REGULATORY INFORMATION

NFPA & HMIS Hazard Ratings:	NFPA		HMIS
	1 Health	0 Least	1 Health
	0 Flammability	1 Slight	0 Flammability
	0 Instability	2 Moderate	0 Reactivity
		3 High	H PPE
		4 Severe	

MATERIAL SAFETY DATA SHEET**ACTIVATOR 90****SARA Hazard Notification/Reporting****SARA Title III Hazard Category:**Immediate Y
Delayed NFire N
Reactive NSudden Release of Pressure N

Reportable Quantity (RQ) under U.S. CERCLA: Not listed

SARA, Title III, Section 313: Not listed

RCRA Waste Code: Not listed

CA Proposition 65: Not listed

16. OTHER INFORMATION

MSDS STATUS: Sections 1 and 4 revised**PREPARED BY:** Registrations and Regulatory Affairs**REVIEWED BY:** Environmental/ Regulatory Services

Disclaimer and Limitation of Liability: This data sheet was developed from information on the constituent materials identified herein and does not relate to the use of such materials in combination with any other material or process. No warranty is expressed or implied with respect to the completeness or ongoing accuracy of the information contained in this data sheet, and LOVELAND PRODUCTS, INC. disclaims all liability for reliance on such information. This data sheet is not a guarantee of safety. Users are responsible for ensuring that they have all current information necessary to safely use the product described by this data sheet for their specific purpose.

Appendix 10: Spray Tracer Purple Label



Spray Tracer

Red and Purple Spray Colorant

GENERAL DESCRIPTION

- Indicates skips and overlaps
- Formulated for compatibility with Roundup® herbicide
- Easy to use

Spray Tracer is a specially blended colorant developed for mixing with Roundup® herbicide to color areas which have been treated, increasing the efficiency of spot treatment applications.

Enhancing placements of pesticides with Spray Tracer produces time and labor savings for the professional applicator. Spray Tracer also helps the applicator meet environmental and product stewardship objectives for their business.

PACKAGING

Available in 12x1 quarts (12x0.95 liters).

RECOMMENDED RATES

APPLICATION	SPRAY TRACER
Spray Marker	1/2 ounce per gallon
Foam Dye	2 ounces per 10 gallons of foam solution

DIRECTIONS FOR USE

Spray Tracer works well in bean bars, cotton riders or similar machines. Spray Tracer also works well as a spray indicator for use in foam marker units as a foam dye.

Color residue is best removed from skin or equipment by rinsing with diluted bleach solution or common (isopropyl) alcohol.

Always be aware and follow any special precautions of these products used in **tank-mix** with Spray Tracer. This product is not compatible with all pesticides. The manufacturer strongly recommends a jar test to determine compatibility with chemicals other than Roundup.

Appendix 11: Spray Tracer Purple MSDS



Material Safety Data Sheet

Section 1. Product and Company Identification

Product Name: SPRAY TRACER PURPLE
Product Code: BUI/SPRAYTPURP
Effective Date: March 26, 2008

Hazardous Material Information System III:

Health	1
Fire Hazard	1
Physical Hazard	1
Personal Protection	X

Manufacturer Information: Becker Underwood, Inc.
801 Dayton Avenue
Ames, Iowa 50010
Information Phone: (515) 232-5907
Emergency Phone: Chemtrec (800) 424-9300

Section 2. Ingredients and Hazards Identification

Hazardous Components		Occupational Exposure Limits		
Component	CAS Number	OSHA PEL	ACGIH TLV	Weight Percent
Acetic Acid*	64-19-7	10 ppm	TWA 10ppm, STEL 15ppm	4-5%
Dipropylene Glycol	25265-71-8	NE	NE	<2%
Basic Violet dye mixture	Proprietary	NE	NE	3-6%
*Acetic Acid is a CERCLA hazardous waste with a reporting quantity of 5000 pounds.				
No reportable quantities of toxic chemical(s) subject to the reporting requirements of Section 313 of SARA Title III and of 40 CFR 372 are present				

Emergency Overview: May cause respiratory tract, eye, and skin irritation.

Potential Acute Health Effects:

Eyes: Irritation may develop causing itching and redness.
Skin: Exposure to unprotected skin areas may cause temporary staining. Mild skin irritation may develop causing itching and redness.
Inhalation: Inhalation of the vapors or mists may cause irritation of the respiratory tract and inflammation of the lungs may result.
Ingestion: Ingestion may cause moderate gastric irritation including nausea and/or vomiting.

Section 3. Composition/Information on Ingredients

The composition of this material is a trade secret. Contains no other components or impurities which will influence the classification with regard to human and environmental risk assessment.

Section 4. First Aid Measures

Eye Contact: Immediately flush eyes with water for at least 15 minutes. Get immediate medical attention.
Skin Contact: Immediately wash affected area with soap and water. Remove and launder contaminated clothing before reuse.
Inhalation: Move to fresh air. Seek medical attention if irritation develops.
Ingestion: Seek immediate medical attention. Dilute with water. DO NOT INDUCE VOMITING.

Section 5. Fire Fighting Measures

Flammability of Product: Not a fire or explosion hazard when stored under normal conditions. At temperatures above 109 F, acetic acid gives off vapors which may form an explosive mixture with air.

Fire Fighting Media: Foam, alcohol foam, CO₂, dry chemical, water fog.

Protective Clothing: No special procedures required besides standard fire fighting procedures.

Section 6. Accidental Release Measures

Clean-Up Procedures: Spills should be contained, solidified and placed in suitable containers for disposal in a licensed facility. Dispose of collected material according to federal, state/provincial and local environmental regulations.

Spills and Leaks: Contain the spill or leak to prevent discharges to surface streams or storm sewers. This material is a concentrated dye/pigment. Small quantities in contaminated water solutions will color large volumes.

Section 7. Handling and Storage

Handling: Avoid breathing fumes. General mechanical ventilation can be expected to effectively remove and prevent build up of any vapor or mist generated from handling this product in a closed environment. Protect eyes to prevent contact. Avoid skin contact.

Storage: Keep container in a dry place inaccessible to children and pets at temperatures above freezing. Keep containers sealed until ready for use.

Section 8. Exposure Control/Personal Protection

Engineering controls: General mechanical ventilation can be expected to effectively remove and prevent build up of any vapor or mist generated from handling this product in a closed environment.

Personal Protection:

Eyes: Wear safety glasses with side shields. Wear additional eye protection such as chemical goggles or face shield if splashing or spraying hazard exists. Have an eye wash station available.

Body: To prevent skin contact wear coveralls, apron, boots, or lab coat.

Hands: Avoid skin contact by using chemically resistant gloves.

Respiratory: Use local exhaust to control excessive vapors/mists. If excessive vapors or mists persist use appropriate NIOSH/MSHA approved organic vapor/mist respirator.

Other: Open wounds or skin surface disruptions should be covered with a chemical resistant patch to minimize absorption risks. Clean clothing should be worn daily to avoid possible long-term build up of the product leading to chronic overexposure.

Section 9. Physical and Chemical Properties

Odor	Acetic acid odor	Vapor Density	Heavier than air
Color	Dark purple	Evaporation Rate	Slower than ether
Physical state	Liquid	Specific Gravity (H₂O = 1)	1.0-1.1 g/mL
pH	3.2-4.2	Solubility	Water soluble
Melting/Freezing Point	NA		

Section 10. Stability and Reactivity

- Chemical Stability:** This material is chemically stable under normal storage and handling conditions.
- Hazardous Decomposition:** When involved in a fire, burning may evolve noxious fumes which may include carbon monoxide, carbon dioxide, nitrous oxides, acetic acid, or other toxic compounds depending on the chemical composition and combustion conditions.
- Hazardous Polymerization:** Is not known to occur.
- Incompatibility (Materials to Avoid):** Long term storage in direct contact with reactive metals such as aluminum, zinc, copper, nickel, magnesium, etc. Other materials to avoid include strong oxidizing agents.
- Conditions to Avoid:** High humidity. Extremes in temperature. At temperatures above 109 F, acetic acid gives off vapors which may form an explosive mixture with air.

Section 11. Toxicological Information

- Chronic Toxicity:** Based on animal data, chronic overexposure to dipropylene glycol may cause liver and kidney damage.
- Mutagenic Effects:** None known
- Teratogenic Effects:** None known
- Developmental Toxicity:** None known
- Acute Effects on Humans:** May cause skin, eye, and respiratory irritation.
- Sensitization:** Repeated or prolonged exposure to the substance at concentration above the exposure limits may cause respiratory tract and lung sensitization.
- Carcinogenic Effects:** Basic Violet 3 (gentian violet) has been determined to cause cancer in rats and mice.
- Existing Medical Conditions Aggravated By Exposure:** May provoke asthmatic response in persons with asthma who are sensitive to airway irritants.

Section 12. Ecological Information

- Ecotoxicity:** No data available, however the material is not expected to have any deleterious toxic effect.
- Environmental Fate:** No data available regarding the environmental fate or biodegradation.

Section 13. Disposal Considerations

EPA Waste Number: Non-hazardous waste

Treatment: Dispose of according to all federal, state/provincial and local environmental regulations.

Section 14. Transport Information

D.O.T. Classification: Not regulated

IMO/IMDG Classification: Not regulated

IATA Classification: Not regulated

Section 15. Regulatory Information

Hazardous Material Information System III:

Health	1
Fire Hazard	1
Physical Hazard	1
Personal Protection	X

Regulatory Listings

United States (TSCA): Listed

Section 16. Other Information

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