ABSTRACT

Title of Document: ASSESSING THE POTENTIAL FOR DOORMATS TO REDUCE PESTICIDE RESIDUES IN THE HOME.

Leanne Marie Ganser, Master of Science, 2006

Directed By: Professor Amy E. Brown, Department of Entomology

This study examined the recommended practice of using doormats at entryways into the home to reduce indirect pesticide exposure. Using doormats to reduce track-in of pesticides is commonly recommended to pesticide applicators, but no studies of the usefulness of this recommendation appear in the literature. The effectiveness of doormats was evaluated by determining the soil levels dislodged from doormats and by determining the ability for laundering to remove pesticide residues embedded into the mats. The performance of three doormat types was assessed. High levels of soil were dislodged from all doormat types. Results from laundering mats showed large variability in the level of residues detected. The results from both studies were influenced by the methods used to test the dislodgeability and effectiveness of laundering. The results of the study suggest further studies are needed to determine the effectiveness of doormats to reduce the potential for pesticide contamination inside the home.

ASSESSING THE POTENTIAL FOR DOORMATS TO REDUCE PESTICIDE RESIDUES IN THE HOME.

By

Leanne Marie Ganser

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Advisory Committee:
Professor Amy E. Brown, Chair
Professor Anugrah Shaw
Professor Galen P. Dively

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Table of Contents

List of Tables

List of Figures

Acronyms Used

AATCC. American Association on Textile Chemists and Colorists

AHS. Agricultural Health Study

CFR. Code of Federal Regulations

EPA. U.S. Environmental Protection Agency

EPC. Environmental Pesticide Control

FIFRA. Federal Insecticide, Fungicide, and Rodenticide Act

GC. Gas chromatography

MS. Mass spectrometry

PPE. Personal Protective Equipment

WPS. Worker Protection Standard

Introduction

Introduction

Since the development of agriculture, humans have looked for methods to protect their crops. Pesticides are an important component of U.S. agriculture. Pesticides are substances used to prevent, destroy or control species that spread disease, damage crops, or are otherwise a nuisance (EPC 2003). Pesticide use is extensive as pesticides aid agricultural workers by increasing yields and farming efficiency (Committee on the Future Role of Pesticides in US Agriculture 2000). A recent report estimated that 888 million pounds of conventional pesticides were used in the US in 2001 for both agricultural and non-agricultural uses, with herbicides accounting for 44% of that market (Donaldson et al. 2004). One estimate suggests the yields of crops would drop by 50% without the crop protection from insects and disease afforded by pesticides (Oerke et al. 1994).

While pesticides are an aid to workers, they may also pose a risk to workers' health and the environment. Acknowledging this risk, the U.S. Environmental Protection Agency (EPA) under the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) is charged with requiring manufacturers to register all pesticides and to study their effects, such as hazards to humans and non-target organisms and the fate of the chemicals in the environment (Title 40 CFR 2005). Across the different classes of pesticides, acute toxic effects greatly vary from non-existent, mild, to severe. The occurrence of such toxic effects after receiving a large dose of a pesticide through an event such as a spill is well documented (Maroni and Fait 1993; Weisenburger 1993; Maddy et al. 1999; He 2000); however, health effects of chronic pesticide exposure continue to be studied.

Pesticide Exposure

Pesticide applicators who are certified to handle pesticides may be exposed to pesticides when mixing, loading, or applying pesticides or when working in treated fields. Pesticide residues present on plants may be transferred onto clothing and skin where the pesticide may be dermally absorbed (Yang and Li 1993; Bernard et al. 2001; Obendorf et al. 2003). Pesticide residues may remain on plants for weeks after application, providing a source of exposure for field workers (Simcox et al. 1999). Non-occupational exposure to pesticides can also occur. Pesticides can be transported into the home where they are distributed into the air and onto surfaces (Nishioka et al. 1999; Lewis et al. 2001). Air is a source of pesticide exposure as pesticide concentrations have been measured inside homes (Roinestad et al. 1993; Lewis et al.1994). Pesticide residues have been found on surfaces inside homes after analyzing surface wipes (Lu et al. 2000; Quandt et al. 2004; Curwin et al. 2005). After contact with surfaces, the residues may be transferred onto the skin (Ivancic et al. 2004) and pesticide may be absorbed dermally or ingested due to hand to mouth action (Simcox et al. 1995; Lu et al. 2000). Exposure may also occur by inhaling airborne pesticides (Lewis et al. 1988; Roinestad et al. 1993).

As pesticides may be present inside the home, family members, along with the pesticide applicator, are at increased risk of pesticide exposure. Pesticides have been associated with long-term effects such as an increased risk of certain types of cancers (Jaga and Dharmani 2005) and birth defects and miscarriages (Arbuckle et al. 2001;

Garry et al. 2002; Hanke and Jurewicz 2004). Of the family members, young children are especially vulnerable to pesticide exposure due to their higher intake of dust and dirt, their proximity to the ground where pesticides have been sprayed and the time spent on low surfaces, such as carpets, which retain dust on the surface fibers (Lewis et al. 1994). Pesticide exposure has been linked to leukemia and other cancers in children (Zahm and Ward 1998). In most cases, the children were exposed as a result of a parent exposed to pesticides occupationally or due to pesticide use in or near the home.

Movement of Pesticides

Pesticides can be brought into the indoor environment through direct indoor spraying, track-in of outdoor pesticides on shoes or pets, or atmospheric transport from outdoors to indoors. One study found that one week after spraying on lawns, the herbicide 2,4-D (2,4-dichlorophenoxyacetic acid) was detected in indoor air and on surfaces throughout the homes (Nishioka et al. 2001). Similar findings were noted by Lewis et al. (2001) after the exterior application of the organophosphate insecticide chlorpyrifos was detected inside the home. Through simulating residential movement by walking over treated turf, Nishioka et al. (1996) determined that track-in of pesticides may be a source of contamination in the home.

The different chemical and physical properties of pesticides influence their behavior in the environment. Some have a tendency to volatilize, and therefore are likely transported through the air, while other pesticides are able bind to soil, which can then be transferred to shoes and pets and deposited on surfaces inside the home. Many pesticides have low vapor pressure or low polarity and therefore have a tendency to partition into soil and dust rather than air (Roberts et al. 1992), suggesting dermal absorption and ingestion of pesticides may be a more significant source of exposure over inhalation.

The extent to which a pesticide will bind to soil depends on the partition coefficient of the individual pesticide. The partition coefficient is the ratio of the amount of pesticide that is bound to soil particles to the amount dissolved in water. The mobility of pesticides is also affected by the soil composition and the pesticide formulation. Sorption of pesticides to soil is greater when the soil contains a high level of organic matter. Pesticide formulations are a mixture of the active ingredient, which is the technical grade of the pure pesticide, and inert ingredients. In liquid formulations, the active ingredient is dissolved in solvents and mixed with water or oil for application as a spray. In dry formulations, the active ingredient is applied to porous materials such as clay. Inert ingredients are added to products for ease in handling and application of the pesticide or for improved effectiveness of the pesticide. Inert ingredients may result in differences in the soil partitioning of liquid and dry formulations.

Pesticide Exposure in the Home

Pesticides present in the home are a concern, as even those who work outdoors spend 10-12 hours a day in the home (Manahan 1997). Pesticide exposure inside homes has been the focus of multiple studies (Simcox et al. 1995; Gladen et al. 1998; Alavanja et al. 1999; Coronado et al. 2004; Curwin et al. 2005). Pesticides were present on surfaces throughout homes examined in central New York, including homes located in agricultural, rural, and urban environments (Obendorf et al. 2006). Residues were often found at the highest levels during the summer months coinciding with the time frame of pesticide application. Overall, higher residues were present in farm homes. Surprisingly, the concentration of pesticides detected indoors is typically greater than outdoors (Lewis et al. 1994). A study of residences in Washington State found concentrations of organophosphorous insecticides ranging from non-detectable to 930 ng/g in soil compared to ranges from non-detectable to 17,000 ng/g in house dust (Simcox et al. 1995). Homes today are typically well sealed in order to reduce energy costs by not allowing heated or cooled air to escape. However, this also prevents pollutants from escaping once they are indoors. Pesticides brought indoors tend to accumulate in the air, on house dust and on surfaces. They are protected from degradation by environmental factors such as rain, sunlight and microorganisms, and thus may have much longer lifetimes indoors than out.

A number of studies consider house dust a potential indicator of long-term pesticide exposure (Roinestad et al. 1993; Lewis et al. 1994; Colt et al. 2004). Roinestad et al. (1993) found that pesticide concentrations in house dust remained relatively constant compared to air samples. House dust can act as a sink for pollutants by absorbing different chemicals depending on the chemical and physical properties of the chemical. Household dust is a complex mixture of biologically derived material, aerosols and soil particles (EPA 1997). It is estimated that house dust is comprised of 30 to 40% outdoor soils (Fergusson and Kim 1991). As outdoor soil constitutes a significant portion of the composition of house dust, the pathway of carrying pesticides into the home by means of soil trapped on shoes and pets requires attention.

A pilot study conducted in North Carolina by the EPA evaluated the pesticide exposure of children to 30 pesticides in house dust, indoor air and outdoor soil.

Pesticides in house dust were found in greater concentrations than concentrations in indoor air and soil (Lewis et al. 1994). A study determined children's exposures were 1,000-10,000 ng/day from contact with floors and 200-30,000 ng/day from contact with tables (Nishioka et al. 2001). The behaviors of children increase the probability of exposure to pesticides. Children frequently put objects or their hands in their mouths, which may have come in direct contact with contaminated surfaces and dust (Simcox et al. 1995). A study of agricultural homes found strong associations between the residue levels found on floors and toys or hand wipes (Quandt et al. 2004). Inhalation of airborne particles is another mode of exposure to pesticides. Examining the distribution of pesticides, a study found that vacuuming and even walking on a carpet resulted in the resuspension of fine particles of dust containing pesticides, which could then be inhaled (Lewis et al. 1999).

Farmers and their families are exposed to more pesticide residues than non-farming families. Studies have shown that pesticide concentrations in urine among the children of farmers and farmworkers are elevated compared to the level in non-farming families (Fenske et al. 2000, Lu et al. 2000). Loewenherz et al. (1997), examining organophorous pesticide metabolites in children in Washington State, found significantly higher levels in the children of pesticide applicators compared to non-agricultural children. Similar levels were determined by Lambert et al. (2005) observing the same metabolites in children of agricultural communities in Oregon. These concentrations may be due not only to exposure in the field, but also to pesticide exposure in the home. In agricultural work, the workplace and the home often share the same location. This presents opportunities for pesticide exposure beyond direct occupational exposure in the field. An increased presence of pesticide metabolites was detected in children living close to treated farmland compared with those agricultural families living greater distances from treated farmland (Lu et al. 2000). A comparison of homes found that pesticides were more frequently detected and higher levels of residues were reported in agricultural homes versus non-agricultural homes (Simcox et al. 1995).

Behaviors Contributing to Pesticide Exposure

Some practices of pesticide applicators, beyond potentially endangering the health of the individual, compromise the health of the family by bringing pesticides into the home. Fenske et al. (2002) documented that pesticides are carried to the indoor environment on clothing and work boots after finding elevated concentrations of chlorpyrifos in homes a significant distance from treated farmland. A study of migrant workers found associations between the distance of the home from treated areas and the number of workers in the home and the level of residues detected suggesting residues are carried into the home by workers (McCauley et al. 2001). Entering the home before removing work clothes (75%) and failing to promptly remove work clothing after entering the home (33%) increased the potential for pesticide exposure in the home in the study by McCauley et al. (2001).

As part of the Agricultural Health Study (AHS), a prospective study of approximately 90,000 pesticide applicators from Iowa and North Carolina, the practices of individuals with incidences of high pesticide exposure were reported. Individuals with documented cases of pesticide exposure events were more likely to participate in practices that could expose other family members to pesticides. Applicators with a self reported high pesticide exposure event were more likely to delay changing work clothing after pesticide application, to wash work clothing with family clothing, to wash up in the home, and to store pesticides in the home, including garage or basement areas (Alavanja et al. 1999). Gladen et al. (1998) found that AHS applicators increased their opportunity for pesticide exposure by mixing pesticides within 50 yards of their home (21%) and storing pesticides in the home (27%). The use of pesticides inside the home increases the likelihood for exposure. In and around the home, farm families in AHS applied non-agricultural pesticides more often than non-agricultural families (Curwin et al. 2002).

Track-in of pesticides

One of the methods by which pesticides are transported from the application site and into the home is by foot traffic. Several studies measuring pesticide residues in the home identified track-in as the primary method of transport for pesticides found in the home (Lewis et al. 2001; Curl et al. 2002; McCauley et al. 2003; Thompson et al. 2003; Curwin et al. 2005). Lewis et al. (2001) suggested track-in as the principal means of pesticide movement in the home after finding chlorpyrifos residues in house dust following an exterior application of the pesticide. Curl et al. (2002) found an agricultural pesticide inside the homes of farmworkers, which indicated that track-in may have contributed to the pesticide contamination. After analyzing house dust from 25 farm and 25 non-farm homes in Iowa for agricultural use only pesticides, residues were detected inside homes and found at the highest levels on floors of the entryway, the changing area, and the laundry room (Curwin et al. 2005) suggesting that residues were tracked in on shoes and were transferred from work clothing deposited onto the floor.

A study of 2,4-D distribution in the home after application found that differences in the activity level of children and pets as well as failure to remove shoes before entering the home contributed significantly to residue levels detected indoors (Nishioka et al. 1999). Examining the transfer of pesticides applied to residential lawns onto carpet, Nishioka et al. (2002) found that track-in occurred over each of the five sampling days of the study. In this study, the pesticides chlorpyrifos and chlorothanil were applied to turf, and participants walked over the treated area onto carpet sections. Carpeted areas in the home typically had higher levels of pesticide residues compared with bare floors (Nishioka et al. 2001; Obendorf et al. 2006). The structure of carpets with a large surface area of fibers enables the carpet to act as a storage reservoir for house dust.

Contact with pesticide-contaminated material

Residues are deposited on clothing while applying pesticide products (Coffman et al. 1999). Bringing contaminated clothing into the home allows for cross contamination with other items. Coronado et al. (2004) determined that the specific job tasks of farmworkers play a role in the level of residue found in the home, suggesting the potential for the transport of pesticides into the home on clothing. Higher levels of pesticide residues were detected in homes where workers waited longer than two hours to change out of work clothes. These workers may also exhibit other behaviors which increase pesticide exposure in the home (McCauley et al. 2003). While farmers recognized that pesticides remained on work clothing after exposure to pesticides in the fields (Branson and Sweeney 1991), a survey of 25 Iowa farm families found that most changed out of their work clothes inside the home and only 12% changed at a location away from the home (Curwin et al. 2002). Seventy-nine percent washed in a bathroom inside the home after applying pesticides.

The person(s) responsible for laundering contaminated clothing can also be exposed to pesticides, potentially absorbing the pesticides dermally from contact with the fabric. A study of applicators found that 94% washed clothing in the same machine as family laundry, although most (81%) washed the contaminated clothing separately in the same machine (Gladen et al. 1998). In a survey of Nebraskan farm families, Tondl and Schulze (2000) found that 81% of the launderers knew if the clothing had been worn for pesticide application. However, despite awareness of the presence of pesticides, only 20% of launderers wore waterproof gloves when handling pesticide-contaminated clothing.

Methods to Reduce Exposure

Reducing exposure from track-in

A study by Nishioka et al. (1996), using the herbicide 2,4-D, found homes that were mostly carpeted showed a high level of the pesticide at the entryway, which decreased farther into the home. Due to this pattern of contamination, the study suggested that a carpeted entry into the home could function as a sink for pesticides that would otherwise be tracked into the home. Nishioka et al. (2002) determined that a polypropylene doormat at an entryway was at least partially effective at reducing track-in, reducing the level of contamination in house dust by 10 to 25%.

The AHS found high compliance with recommended practices to reduce the track-in of pesticides on shoes, including placing a doormat at entryways and removing shoes before entering the home (Gladen et al. 1998). Ninety-three percent of families enrolled in the study reported having a mat at the door to clean soil from shoes. Sixty-two percent reported that family members removed shoes before entering the house after working in the fields. However, another survey found only 36% of farm workers removed their shoes before entering the home, providing an opportunity to track residues into the home (Curwin et al. 2002).

Reducing exposure from clothing

Laundering is typically used to remove pesticide residues from clothing. In common fabrics, the removal of pesticides by laundering ranged from 1% to over 42% remaining in the fabric depending on the pesticide and fabric used (Nelson et al. 1992). Differences were found in the removal of pesticide among the pesticide chemical classes used in the Nelson study. Pesticide formulations also may affect the effectiveness of laundering. Emulsifiable concentrations tend to be more difficult to remove from fabric than flowable liquid formulations (Easter and DeJonge 1985). Heavy-duty liquid detergent formulations are most efficient in removing emulsifiable concentrations from fabric as they are effective on oil based stains (Laughlin 1993). Park et al. (1990) did not find a significant difference between detergents in the removal of emulsifiable concentrate formulations of parathion and methyl parathion. Levels of pesticide remaining in un-weathered samples after laundering ranged from 40 to 46% for parathion and 22 to 25% for methyl parathion (Park et al. 1990).

Perception of Risk

Misperceptions about the toxicity of pesticides may lead to a disregard for safety measures. As part of the Preventing Agricultural Chemical Exposure in North Carolina Farmworkers' Project, Arcury et al. (2002) found that more than 20% of workers interviewed thought pesticides did not present harm to themselves or their families. Only 5% of interviewed North Carolina workers felt that their clothing provided any control over their pesticide exposure. Similarly, 54% of these workers believed laundering clothing provided no additional control over the extent of pesticide exposure. The farm workers displayed different perceptions as to their exposure to pesticides depending on what task they performed.

Pesticide safety training is extremely important to ensure safe usage of pesticides. Applicators can significantly reduce occupational exposure to pesticides by using personal protective equipment (PPE) (Branson and Sweeney 1991). Workers with knowledge of pesticide safety practices are more inclined to comply with PPE requirements (Perry et al. 2000). Pesticide safety training is also an opportunity to educate agricultural workers on ways to reduce indirect exposure to pesticides. In a study of dairy farmers in Wisconsin, Perry et al. (2000) found that possessing knowledge important for using pesticides safely was associated with confidence among farmers that they could prevent the exposure of self and family to pesticides. Farmers surveyed by Perry et al. (2000) showed gaps in safety knowledge and reported less than optimal knowledge scores. Thompson et al. (2003) found workers who participated in the mixing, loading or application of pesticides where more likely to follow good hygienic practices, such as washing hands after work and laundering work clothing after one wearing, compared to other farmworkers. Many pesticide applicators must be certified in order to perform their job. The training required includes information on preventing pesticide exposure, which may account for differences in the behaviors of farm workers with and without pesticide training.

Educational Efforts

Most educational programs focus on the potential risks of pesticide exposure and methods of protection from exposure while working in the field. The usage of PPE by agricultural workers increases with awareness of methods of protection from exposure (Perry and Layde 2003). A comparison of pesticide exposure in applicators using their typical PPE with pesticide exposure after they had been given a sized-to-fit full-face respirator, long gloves, chemical proof boots and a Tyvek ® hood determined dermal exposure levels decreased about fourfold after the additional PPE was used (van der Jagt et al. 2004). Such interventions to educate pesticide handlers as to the increased risk of pesticide exposure due to their behaviors have resulted in some increases in PPE usage. Perry and Layde (2003) performed educational sessions to educate farmers on evidence of increased cancer rates among farmers, simulating pesticide exposure methods, reporting data collected on exposure and explaining behaviors to reduce pesticide exposure. Although the education did not increase full PPE compliance, Perry and Layde reported significant elevation in the odds of using gloves or any other gear in the most recent application following the intervention.

Interventions aiming to change the behavior of agricultural workers are typically done on a small scale, involving a few communities. A study by a student in the Entomology Department at the University of Maryland determined behaviors contributing to pesticide exposure and practices to reduce exposure in the home as well as in the field (Clark 2004). The inquiry did not find a significant change in behavior due to intervention; however, many of the applicators were already employing recommended or acceptable handling practices. Recommended practices included the use of PPE by the applicator and methods to reduce exposure in the home. As pesticides can be brought into the home though track in, recommended practices included the use of a throw rug inside the entryway to trap pesticides, and removing shoes before entering.

A large-scale educational effort was introduced in 1992 with the Worker Protection Standard (WPS) providing a set of regulations from the EPA to protect agricultural workers from excessive pesticide exposure. These rules include restrictions on who can be in the field when pesticides are being applied, the time period before workers can reenter the treated area, and notification that an area has been treated in order to avoid exposing workers to pesticides. Other safety measures involve requirements for PPE use, availability of decontamination supplies, and emergency assistance. Handlers must have access to labeling information on the pesticides being used. To make sure that the pesticides will be handled properly, the WPS requires pesticide safety training for all pesticide handlers and workers on farms, greenhouses, and nurseries or in foresting operations.

Rationale for Study

This study examined a recommended practice suggested to reduce indirect pesticide exposure. As many farm homes are close to the pesticide application sites, opportunity for track-in and indirect exposure to pesticides exists. Hygienic practices such as promptly removing work clothing, removing shoes at the door, and using doormats at entryways have been suggested in order for homeowners to reduce the presence of pesticide residues in the home (Lewis et al. 1994; McCauley et al. 2003; Clark 2004). AHS questionnaires included the use of doormats in evaluating the hygienic practices of farmers (Gladen et al. 1998; Curwin et al. 2002; Curwin et al. 2005). In addition to the recommendation for the use of a doormat at entryways to reduce track-in, laundering of the doormat was also noted in the recommendations by Clark (2004) as important in order to prevent any accumulated residues from continuing to be tracked into the home. However, there is currently no published literature on the ability of laundering to remove accumulated pesticide residues from doormats.

As dislodged soil and carpet fibers from doormats are potential sources of contamination for the household if pesticide residues are bound to them, the study incorporated three types of doormats to determine the ability for pesticide residues to be dislodged from doormats with direct pressure, which may occur when walking across the mat. The study also examined the potential for washing to remove residues from the mats, and thus prevent pesticide residues from accumulating within the mats.

Objectives

1. Determine the potential for soil to be dislodged from different types of doormats.
2. Evaluate the potential effectiveness of laundering to remove pesticide residues from different types of doormats.

Materials and Methods

<u>Overview of the Study</u>

To determine the potential effectiveness of doormats in reducing pesticide contamination in the home, two experiments were performed: 1.) the dislodgeability of soil from three different types of doormats, and 2.) the effect of laundering on three different types of doormats contaminated with soil treated with an emulsifiable concentrate pesticide formulation of chlorpyrifos (Lorsban 4E).

After an informal survey of doormats available at home supply stores, three types of mats were chosen with different fiber content and construction based on availability and care instructions. Cotton woven, nylon loop pile, and polypropylene loop pile mats, doormat types A, B, and C respectively, were evaluated in this study for the ability of pesticide residues to be dislodged by direct pressure and to be removed by laundering. Mats for which instructions recommended dry cleaning or spot cleaning treatments were not included in this study, as the premise for the study was that home laundering of the doormats would reduce a potential source of pesticide contamination in the home. Other mat types not studied included outdoor use only mats that recommended cleaning by shaking, including heavy rubber mats and doormats made of coir fibers. The soil available for track-in into the home was determined by embedding soil into mat types A, B, and C, and then vacuuming. A completely randomized design was used for the study examining the difference between mat type and the dislodgeability of soil. Another set of A, B, and C mats were contaminated with a mixture of soil and pesticide and laundered to determine the ability of laundering to remove pesticides from the mats. A 3 x 2 factorial design was used for the study. The two factors were mat type and laundering.

Lorsban 4E, an emulsifiable concentrate pesticide formulation with an active ingredient of chlorpyrifos, was chosen as the indicator pesticide. Chlorpyrifos, an organophosphate insecticide, is widely used in agriculture and is labeled for use at a reasonably high rate. Soil for the experiment was treated with an amount of pesticide similar to the level applied in the field.

Properties of Chlorpyrifos

Chlorpyrifos (Figure 1), an organophosphate insecticide, is widely used in agriculture. Trade names for the pesticide include Dursban®, Lorsban®, Empire 20®, Equity®, and Whitmire PT270® (EPA 2002a). Due to its usage as an agricultural pesticide only and the detection of chlorpyrifos within homes (Colt et al. 2004; Lu et al. 2004; Curwin et al. 2005), chlorpyrifos represents a potential contaminant that may be tracked from agricultural sites into the home. Chlorpyrifos is applied for agricultural purposes each year at the rate of about 10 million pounds in the U.S. (EPA 2002b). For

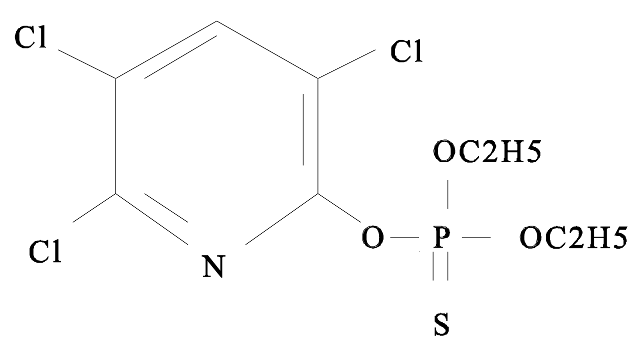


Figure 1. Chemical structure of chlorpyrifos

application to field crops, rates vary, but are typically in the range of 0.25 - 3 lb active ingredient per acre. Chlorpyrifos was used as a residential insecticide until 2001, when its residential use was terminated due to health risks (EPA 2002b).

Chlorpyrifos is found mainly in the air and soil once released into the environment after application. Volatilization is the primary means by which the insecticide is dispersed after application. A large quantity of the chlorpyrifos applied to foliage will eventually reach soil. Chlorpyrifos has the potential for transport into the home through track-in, as it will bind strongly to soils, having an average organic carbon partition coefficient of 8498. It is immobile in soil and will not leach into water. However, its major degradation product, 3,5,6-trichloro-2-pyridinol (TCP), is more mobile and persistent in soils (Racke 1993).

Studies on the fate of chlorpyrifos in the environment found only very low levels of the insecticide taken up by plant roots or metabolized by cranberry bean plants (Kenaga et al. 1965; Smith et al. 1967). Other studies on cauliflower and brussel sprouts found that chlorpyrifos was transported from soil into the plant foliage (Rouchaud et al. 1991). In soil, chlorpyrifos is slowly degraded by hydrolysis and microbial action. Depending on soil type and temperature, chlorpyrifos displayed a half-life of less than 3 weeks to greater than 24 weeks (Risher and Navarro 1997). Data on field dissipation showed the insecticide is moderately persistent, having a half-life of 33 to 56 days in cornfield soil (EPA 2000).

Preliminary Work

Determining soil characteristics

As this study examined the track-in of pesticides bound to soil that may occur at homes where soil can be brought in from farms, soil used in the study was taken from a soybean plot at Nick's Organic Farm (Potomac, MD). Soil available at this location would likely be similar to soil present in other nearby agricultural regions and had not been treated with pesticides for over 10 years. The soil was a Glenelg-Manor silt loam soil. Silt loam soils contain more than 50% silt. An independent soil analysis performed by A&L Eastern Agricultural Laboratories (Richmond, VA) in 2004 provided data on various nutrient levels in the soil (Appendix 1). The level of organic matter was 2.2%, which was noted as a medium level, and the soil pH was 5.7. The soil was mixed thoroughly and sieved to remove debris and large particles to obtain a consistent soil mixture.

To determine whether any detectable background level of chlorpyrifos was present in the soil, three 5 g soil samples were taken and extracted following a procedure modified from Simcox et al. (1995). The 5 g soil samples were placed in Erlenmeyer flasks and mixed with 2 ml of distilled water. The samples were stored at 4°C for 15 h. Fifty ml acetone was added to the Erlenmeyer flasks and the samples were shaken on a wrist action shaker for 1 h. The solution was filtered using a Buchner funnel to separate the supernatant from the soil solids. The supernatants were evaporated to near dryness using a gentle stream of nitrogen and partitioned between 2 ml hexane and 40 ml water. The hexane layer was separated and dried over anhydrous sodium sulfate. The extracts were stored in GC/MS vials at 4°C until analysis by GC/MS.

Determining appropriate soil quantity

To determine a reasonable amount of soil to apply to the mat, soil similar to the type previously described was loaded into the grooves of the sole of a work boot by pressing the boot into a tub containing moist soil. This provided an estimate of the maximum quantity of soil tracked onto the mat at one time. The soil was moistened by adding 100 ml of water to 500 g of the soil. After mixing the water and soil, the boot was pressed into the mixture 10 times to cover the bottom of the boot. After applying the soil to the boot, the soil was allowed to dry overnight on the boot and then dislodged by scraping the soil from the boot with a metal spatula until it appeared that no more soil could removed. This procedure was repeated 5 times and the average amount of dislodgeable soil was calculated.

Two soil contamination levels were assigned. One half of the average of the amount dislodged was used to contaminate the mats for the dislodgeability experiment with the high contamination level, as if this boot were contaminated in a true setting the soil would likely be spread over twice the area of the mat sections used for this experiment. One fourth of the amount of dislodged soil was used to contaminate the mats for the dislodgeability experiment with the low contamination level. Mats for the laundering experiment were contaminated with one fourth of the amount of dislodged soil.

Determining appropriate level of pesticide contamination in soil

A study by Singh et al. (2002), which treated soil with chlorpyrifos to examine pesticide degradation, selected the lowest dose of chlorpyrifos used in agriculture in the United Kingdom. The lowest dose (10 mg/ kg) was noted as equivalent to 1.0 kg/ha of chlorpyrifos incorporated to a depth of 1 cm in the soil. Following this methodology, the level to contaminate the experimental soil with chlorpyrifos in this study was determined using the highest labeled rates for Maryland agriculture. The formulation Lorsban 4E was chosen due to its widespread use on crops. The highest labeled rate on corn is 0.75 gal formulation per acre. The equivalent amount of mg active ingredient per kg soil was determined. Three pounds of the active ingredient chlorpyrifos is contained in 0.75 gal of formulation. To incorporate soil depth into the calculations, the weight of 1 cm^3 soil was found by weighing 10 ml soil and dividing the result by ten. This procedure was performed five times and the average weight was calculated. The average weight of 1 cm^3 soil was used to determine the weight of soil in one acre. Thirty-nine milligrams chlorpyrifos per kg soil was determined as equivalent to 0.75 gal of formulated product per acre.

Eight hundred grams of soil treated with 31.2 mg chlorpyrifos or 67 μL Lorsban 4E would achieve a ratio of 39 mg ai/kg soil. This would result in a level in the treated soil that could be found in a field after the highest labeled rate of Lorsban 4E was applied. In addition to walking through treated fields, applicators often mix and load the pesticide into their equipment. Areas used for mixing and loading tend to be contaminated at a higher level than treated fields, and applicators would likely pick up a higher amount of residue from these areas. Studies by Habecker et al. (1989) and

Helweg et al. (2002) have found that in areas where pesticides are mixed and loaded into equipment before pesticide application, pesticide levels in soil are above those of labeled rates due to small spills and cleaning of equipment. Habecker et al. (1989) found pesticide concentrations in soil 2 -75 times higher than labeled rates. Parathion, the only organophosphate measured, was found in the soil at 75 times the highest labeled rate. To account for the higher concentration for chlorpyrifos that could be tracked into the home on shoes, a conservative level of 335 μL Lorsban 4E, or five times the previously determined amount, was used to treat 800 g soil.

Treatment of soil with pesticide

Eight hundred grams of soil was weighed and placed in a round metal pan. Three hundred and thirty-five microliters Lorsban 4E was pipetted into a beaker containing 500 ml distilled water. The solution was stirred to distribute the pesticide evenly in the water. The solution was poured over the soil and thoroughly mixed with a metal spatula. The pan was placed in a fume hood and the excess water was allowed to evaporate. The pan was turned every 4 hours to ensure consistent drying of the soil. The soil was stored at 4°C each night to prevent drying of the soil when it was not monitored. After 64 h, the treated soil was transferred to a glass beaker and stored at 4°C. Three samples were taken from the treated soil to determine percent moisture. The samples were weighed, allowed to air-dry overnight and reweighed.

Three samples were taken from the contaminated soil mixture to determine that the soil had been evenly contaminated with chlorpyrifos to the level of 0.2 mg/g. The 5 g soil samples were placed in Erlenmeyer flasks and mixed with 2 ml of distilled water.

The samples were stored at 4°C for 15 h. Fifty ml acetone was added to each Erlenmeyer flask and the samples were shaken on a wrist action shaker for 1 h. The solution was filtered using a Buchner funnel to separate the supernatant from the soil solids. The supernatants were evaporated to near dryness using a gentle stream of nitrogen and partitioned between 2 ml hexane and 40 ml water. The hexane layer was separated and dried over anhydrous sodium sulfate. The extracts were stored in GC/MS vials at 4°C until analysis by GC/MS.

Properties of Doormats

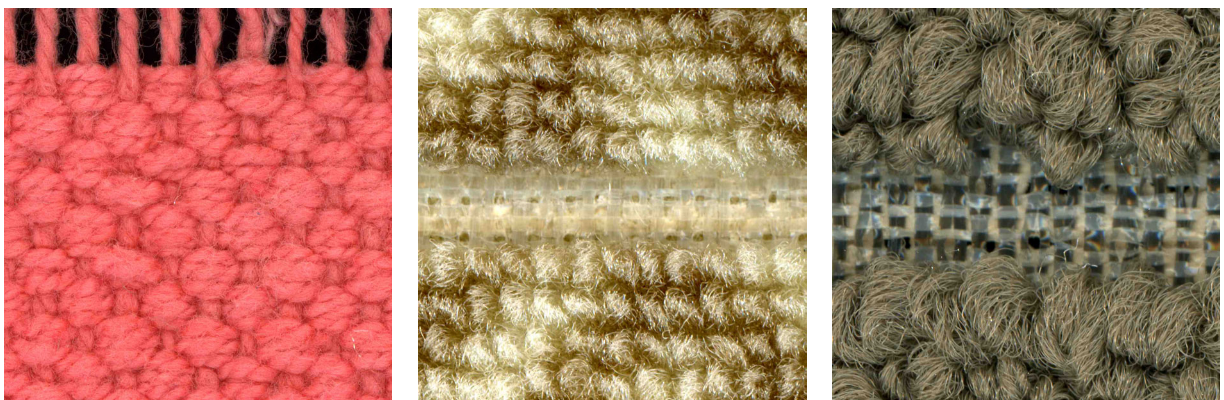
Two mats constructed of synthetic fibers (B and C) and one mat of natural fibers (A) were chosen for the experiment (Table 1, Figure 2). The mats varied in their construction with mats B and C being most similar. Type A was constructed of cotton yarns, which formed a woven mat (Figure 3, Figure 4). Mat A did not have a backing. Mats B and C had a rubber backing. Type B and C had a loop pile construction with loops of nylon and polypropylene fibers, respectively (Figure 3, Figure 4).

Table 1: Doormat characteristics

Mat type	Fiber Content	Construction	Backing	Pile Height (cm)
A	100% cotton	woven	no	n/a
B	100% nylon	tufted (loop pile)	yes	0.29
C	100% polypropylene	tufted (loop pile)	yes	0.40 and 0.50 alternating every other row

A B C

Figure 2: Doormat Types



A B C

Two rows of tufted yarns pulled from type B and C to expose the mat backing.

Figure 3: Doormat construction

A B C

Figure 4: Yarns from doormats

Preparation of doormats

To remove manufacturer's sizing, mat types A, B, and C were laundered once according to the manufacturer's label, using a modified AATCC Test Method 143-1996 (AATCC 2001a). Modifications include the use of Tide ®, cold/cold water temperature setting, and no addition of ballast material. The mats were line dried overnight.

Dislodgeablility Experiment

Three sections were acquired from each mat type by using a template to cut 30 cm x 20 cm specimens from the mats. The three sections were randomly numbered 1 - 3.

Soil used for the experiment was obtained from Nick's Organic Farm in Potomac, Maryland. The soil was moistened to a level similar to the level used in the laundering experiment by mixing 300 ml of water with 700 g clean soil in a round metal pan. The soil was placed in a fume hood and allowed to air dry, periodically taking a 5 g soil sample to determine the percent moisture. The soil was stored in a glass beaker at 4°C until use. Clean soil was applied to each mat section by using a hand sifter to distribute the soil evenly over the mat surface and each mat specimen was treated as follows (Figure 5):

- Section 1: 20 g clean soil for a high level of contamination was sifted onto the section
- Section 2: 10 g clean soil for a low level of contamination was sifted onto the section

– Section 3: no soil was sifted onto the section

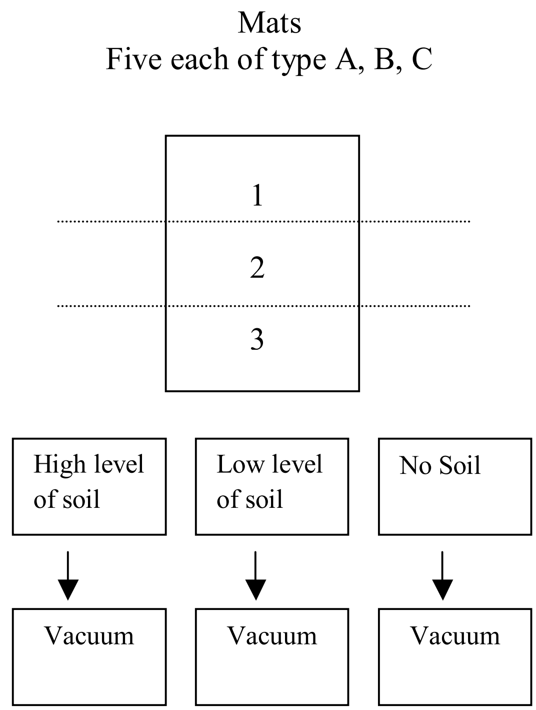


Figure 5: Preparation of mats for collection of dislodgeable residues

To simulate the action of shoes rubbing against the mat, the soil was embedded into the mat using a foot press. The investigator pressed with a shoe-covered foot onto the mat for the basic apparatus of the foot press. A neoprene sheet was taped to the bottom of the shoe to prevent residues from adhering to the shoe. The investigator placed the ball of the foot on one corner of the mat and moved across the rug pressing and using only the ball of the foot when twisting the shoe once to each side before lifting the foot and proceeding along the mat once length-wise and then once width-wise.

After embedding the soil into the mat specimens, the portion of soil dislodged was measured by vacuuming the mat sections. The soil collected allowed for an estimate of how much soil is available for track-in into the home. Although the soil used for this study was not contaminated, the amount of pesticide residue that would be tracked in using the contaminated soil was determined, to provide an estimate of the degree of pesticide track-in, given the initial amount of contamination used for the laundering experiment.

To determine the portion of soil and carpet fiber able to be dislodged, the mat sections were vacuumed using the HVS4, the latest version of the High Volume Small Surface Samplers originally developed for use by the EPA for collection of house dust (CS3, Inc. 1998). The HVS3 has been successfully used to collect house dust samples for analysis of pesticide residues (Simcox et al. 1995; Colt et al. 1998; and Fenske et al. 2002). The updated HVS4 is lighter than the traditionally used HVS3, utilizes a canister vacuum instead of an upright vacuum, and is less expensive to purchase. Dust enters the HVS4 through the nozzle and travels into the cyclone where particles greater than 5 μm are captured. The vacuum cleaner was adjusted according the calibrations in the HVS4 manual.

Each doormat section was affixed to the floor using double-sided tape to prevent the mat from moving while vacuuming. The HVS4 was moved over the surface for a series of four passes back and forth. After vacuuming each section, the collection bottle was removed from the vacuum and labeled for gravimetric analysis.

The experiment was repeated 4 more times for 5 replicates of each treatment combination.

Statistical analysis of dislodgeable residues

The data from this completely randomized design were analyzed by performing an analysis of variance (ANOVA) to determine if a difference exists between the amount of soil dislodged and the three types of mat fabric. A statistical package (SAS ® Cary, North Carolina) was used to analyze the data (SAS Institute Inc. 2004).

Laundering Experiment

Two sections were obtained from each mat of each fabric type (Figure 6). The sections were acquired by using a template to cut 15 cm x 20 cm specimens from the mats. The sides of the type A mats were sewn using a zigzag stitch to prevent unraveling during laundering.

All sections obtained from each mat were contaminated with chlorpyrifos-treated soil. The contaminated soil was applied to the mat specimens by using a hand sifter to distribute the soil evenly over the mat surface. Ten grams was sifted onto each mat.

To simulate the action of shoes rubbing against the mat, the soil was embedded into the mat using a foot press. The investigator pressed with a shoe-covered foot onto the mat for the basic apparatus of the foot press. A neoprene sheet was taped to the bottom of the shoe to prevent residues from adhering to the shoe. The investigator placed the ball of the foot on one corner of the mat and moved across the rug pressing and using only the ball of the foot when twisting the shoe once to each side before lifting the foot and proceeding along the mat once length-wise and then once width-wise.

Mats
Ten each of type A, B, C

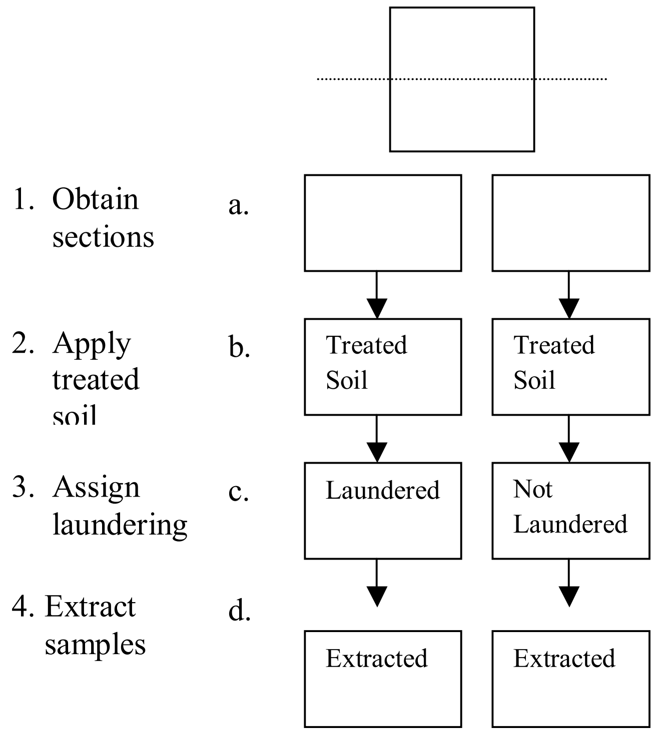


Figure 6: Preparation of mats for collection of removable residues

After embedding the soil into the mats, one of the two sections from each of the 10 mats contaminated with the pesticide-soil mixture was assigned laundering. The sections were laundered following a modified 61-1996 method of the AATCC (AATCC 2001b). Each mat specimen was laundered once, separately, in a 1200 ml steel can with 800 ml of soap solution, using Tide ® a granular detergent which contains an anionic surfactant and produces an alkaline solution in water, adding 20 steel balls for agitation, at 40°C for 10 minutes using a launder-o-meter. Afterwards, the sections were rinsed twice with 800 ml of distilled water and allowed to line dry at room temperature. Finally, the sections were wrapped in aluminum foil, placed in sealed bags, labeled and stored at

4°C until extraction. The study was repeated nine more times, resulting in 10 replicates of each treatment combination and a total of 60 experimental units.

Residue extraction

Each 20 cm x 15 cm mat sample was sprayed with 2 ml of distilled water to wet the surface and stored at 4°C for 15-17 h. Each mat sample was cut into 6 squares and placed in a 1000 ml Erlenmeyer flask. Five hundred ml acetone was added to the flask and the flask was attached to a wrist action shaker. The sample was allowed to shake for 1 h, after which the mat squares were rung out with forceps and transferred into aluminum foil for storage at 4°C. A Buchner funnel was used to filter the supernatant from the soil solids and carpet fibers. The supernatant was evaporated to near dryness using a rotary evaporator. The supernatant was partitioned between 2 ml hexane and 40 ml water. The hexane layer was separated, centrifuged 15 min and any additional water was removed. Two ml acetonitrile was added to the hexane and centrifuged 15 min. The acetonitrile layer was stored in a test tube at 4°C before clean-up step.

To clean the sample, a florisil procedure used by Clark (2004), similar to the procedure developed by Putnam et al. (2003), was used. The SPE florisil cells were placed in a chamber. Three ml of hexane were added to the SPE cell. One g of sodium sulfate was added on top of the hexane in the cell. The gauge was adjusted to allow the formation of a vacuum to pull the hexane into the chamber reservoir in a drop-wise manner. Next, the lid was removed from the chamber and a rack of centrifuge tubes was placed in the chamber reservoir. A 1 ml aliquot of the concentrated sample from the test tube was pipetted into the cell. Three ml of hexane was added to the cell and a vacuum was used to pull the sample through the cell in a drop-wise manner. Five ml of 20:80 hexane:acetone was added to each cell and pulled through the cell in a drop-wise manner. The solution in the centrifuge tube was then reduced to 1 ml under a nitrogen stream. The concentrate was solvent exchanged into hexane and reduced to 1 ml under a nitrogen stream. Finally, the concentrate was filtered using a 0.45 um nylon screen attached to a hypodermic glass syringe. The concentrate from non-laundered samples was diluted by removing 0.10 ml aliquot and adding acetonitrile to return the volume to 1 ml. This solution was injected into a GC/MS vial and stored at $4^{o}C$ until analysis. Analysis of the sample was performed using GC/MS.

Pesticide residue analysis

Preparation of standard solutions

Stock solution of 10 mg of chlorpyrifos per 10 ml of hexane was prepared. Aliquots of the stock solution were diluted in hexane for use as working standard solutions. Two calibration curves for the standard solution were generated to account for the curve of the line as the detector neared saturation (Figure 7). Best fit lines were fitted to the data points.

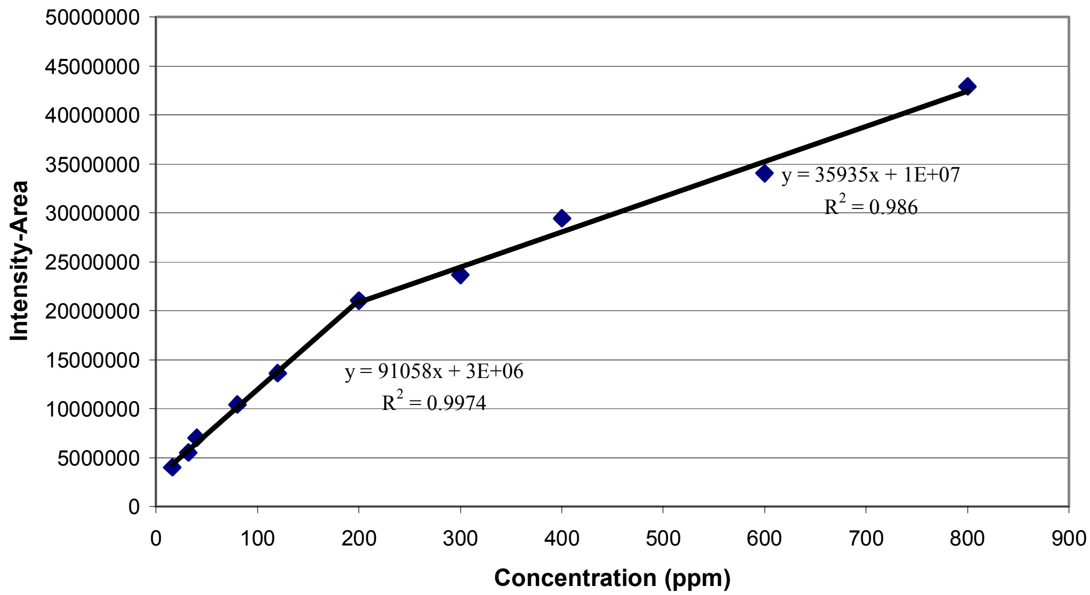


Figure 7. Calibration curves prepared from a stock solution of 10 mg of chlorpyrifos per 10 ml of hexane.

Analysis of residues

The samples were analyzed using gas chromatography (GC) and mass spectrometry (MS). All the samples were analyzed for chlorpyrifos.

For all samples, the AS9000 autosampler method was used, with a sample volume of 1 ul and appropriate washes in between samples. The capillary column was a 5% phenyl polysiloxane ZB-5, 30 m x 0.25 mm x 0.25 um film thickness. The analysis used splitless injection. The injection temperature was 250°C. The oven temperature program consisted of an initial value of 60°C held for 1 min ramped at 20°C/min to 290°C and held for 1 min for a total of 13.5 min. The carrier gas was helium at a rate of 40 cm/sec.

The mass spectrometer was operated in positive mode using a full scan from 50-400 atomic mass units. The source temperature was 200°C and the transfer line was 275°C. The start time was 3 min.

Statistical analysis of residues removed by laundering

Two factors were evaluated to determine their effect on the amount of pesticide removed. The treatment factors included the type of mat and laundering of the mat. To test the multiple factors, a factorial treatment design was constructed. A statistical package (SAS ® Cary, North Carolina) was used to analyze the data from this completely randomized design with a factorial treatment structure (SAS Institute Inc. 2004). The data were analyzed by performing an analysis of variance (ANOVA).

Results

Soil Treatment

Analysis of soil from Nick's Organic Farm showed no detectable levels of chlorpyrifos. Soil for the laundering experiment was treated with a mixture of chlorpyrifos and water. After treating the soil, the percent moisture of the soil was 23.53 ± 0.33. The concentration of chlorpyrifos in the soil after treatment was 0.075 ± 0.009 mg/g. As the soil was well mixed after treatment, the levels were determined sufficiently consistent to proceed with the laundering experiment. Untreated soil from Nick's Organic Farm was used for the dislodgeable experiment. After adding water to the soil, the percent moisture of the soil was 28.17 ± 0.29.

Dislodgeable Experiment

Summary concentration data are shown in Table 2. Raw data can be found in Appendix Tables 1-3. Statistical data can be found in Appendix Tables 4 and 5.

The amount of soil dislodged by vacuuming from the mats with 10 g of soil embedded ranged from 5.31 to 8.16 g (Table 2). From the mats with 20 g of soil embedded, 10.77 to 16.99 g of soil was dislodged. Approximately 69% and 73% of soil from the low level and high level of soil embedded, respectively, was dislodged (Figure 8, Figure 9). Using the level of pesticide contamination added to the soil for the laundering experiment (0.075 mg/g), the amount of pesticide that would have been dislodged in the experiment was calculated. For mats with a low level of soil added, the amount of chlorpyrifos potentially available for transfer into the home ranged from 0.40 to 0.46 mg. For mats with a high level of soil embedded, the potential amount of chlorpyrifos for transfer was 0.81 to 1.27 mg.

Table 2: Amount (g) of soil dislodged from doormats

Amount of Soil Embedded	A	B	C	All Mat Types
10 g soil	7.12 ± 0.87	7.35 ± 0.48	6.1 ± 0.78	6.86 ± 0.88
20 g soil	15.35 ± 1.37	15.52 ± 0.82	12.8 ± 1.32	14.56 ± 1.70
Mean ± standard deviation				

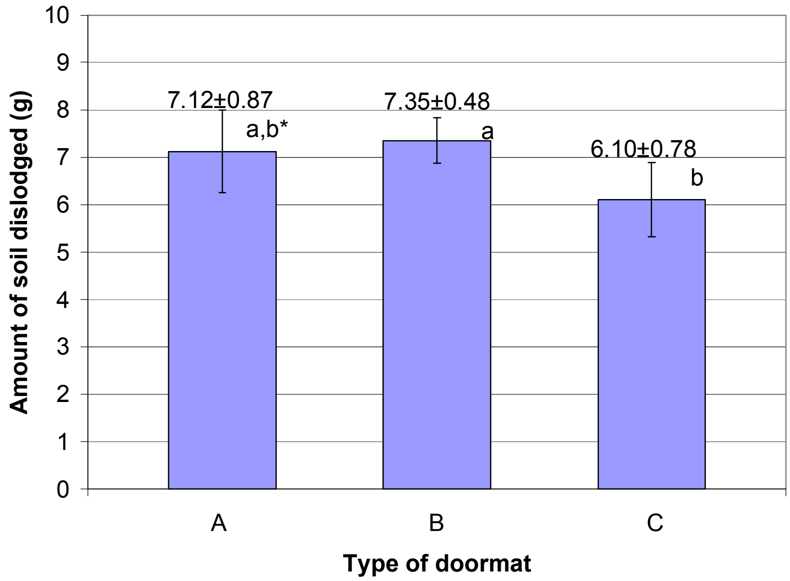


Figure 8: Amount of low level of soil (10 g embedded) dislodged from doormats

*Means sharing any letters are not significantly different

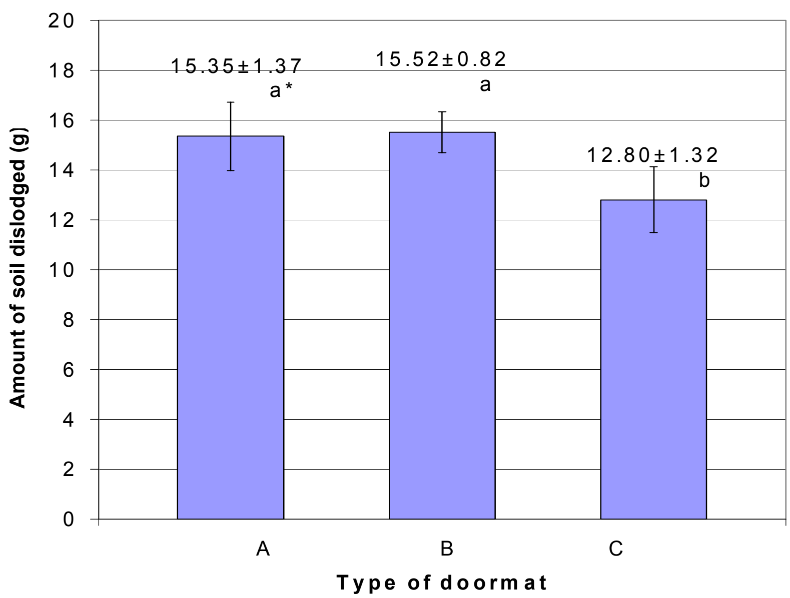


Figure 9: Amount of high level of soil (20 g embedded) dislodged from doormats

*Means sharing any letters are not significantly different

A one-way analysis of variance was performed using the mixed procedure. The t-test probabilities were determined for pairwise mean comparisons. The main effect of mat type was significant at the high level of soil ($F_{(2,12)}$ = 8.14, p=0.006) and at the low level of soil ($F_{(2,12)}$ = 4.13, p=0.043). The amount of soil dislodged from A and B doormats was similar. There was no significant difference between A and B mats at either the high (*t*=-0.22, p=0.83) or the low (*t*=-0.50, p=0.628) level of soil. At the high level of soil application, 77% and 78% soil was dislodged from mat types A and B, respectively. At the low level of soil application, 71% and 73% soil was dislodged from mat types A and B, respectively. The dislodgeability from mat type C was significantly different from mat types A (*t*=3.38, p=0.006) and B (*t*=3.60, p=0.004) with the high level of soil, where approximately 64% of soil was dislodged. At the low level of soil, type C was significantly different from type A (t=2.20, p=0.048) and from type B (t=2.70, p=0.019) where approximately 61% of soil was dislodged. There was no significant difference among the mats with no soil added ($F_{(2,12)}$ = 0.38, p=0.692) as a similar amount of mat fibers and yarns were dislodged.

Laundering Experiment

Summary concentration data are shown in Table 3. Raw data can be found in Appendix Tables 6-8. Statistical data can be found in Appendix Tables 9 and 10.
The concentration of chlorpyrifos applied to the doormats was 750 ppm. The recoverable chlorpyrifos concentration in laundered doormats was 331 ± 221 ppm and in non-laundered doormats was 519 ± 244 ppm. The aggregate amount of residue remaining in

the laundered mats was 44% compared with 69% remaining in the non-laundered mats to which no further treatment was performed after embedding the soil. The level of chlorpyrifos residue recovered from the mats was widely variable among the doormats (Figure 8). The levels of chlorpyrifos in the non-laundered doormat types A, B and C were 479 ± 250, 416 ± 200, and 663 ± 192, respectively (Figure 8). A two-way analysis of variance was performed using the mixed procedure. The t-test probabilities were determined for pairwise mean comparisons. The two-way analysis of variance yielded a main effect for mat type that was statistically significant ($F_{(2,54)} = 7.41$, p=0.001). The main effect of laundering was also significant ($F_{(1,54)} = 13.49$, p<0.001). The interaction between mat type and laundering was significant ($F_{(2,54)} = 5.25$, p=0.008); therefore, the main effects should not be interpreted alone. No significant difference was detected between the non-laundered type A and B doormats (*t*=0.71,p= 0.48). However, detection in the non-laundered type C doormats was significantly different from the detection in non-laundered type A doormats (*t*=-2.07, p=0.043) and non-laundered type B doormats (*t*=-2.78,p=0.007).

Table 3: Concentration (ppm) of chlorpyrifos extracted from doormats

	A	B	C	All Mat Types
Non-Laundered	479 ± 250	416 ± 200	663 ± 192	519 ± 244
Laundered	120 ± 47	453 ± 195	419 ± 184	331 ± 221
Mean ± standard deviation				

The laundered type A doormats showed the lowest variability among samples. The laundered type A mats also gave the lowest concentrations of chlorpyrifos (120 ± 47 ppm) (Table 3). Only 16% of the residue remained in the type A mats after laundering. The laundered type A mats retained significantly less chlorpyrifos than type B (*t*=-3.74, p<0.001) and C (*t*=-3.36, p=0.001) doormats after laundering. The levels of chlorpyrifos remaining in type B and C doormats after laundering were similar to each other (*t*=0.38, p=0.704). The concentration of chlorpyrifos in laundered type B doormats was 453 ± 195 ppm and in laundered type C doormats was 419 ± 184 ppm (Figure 8).

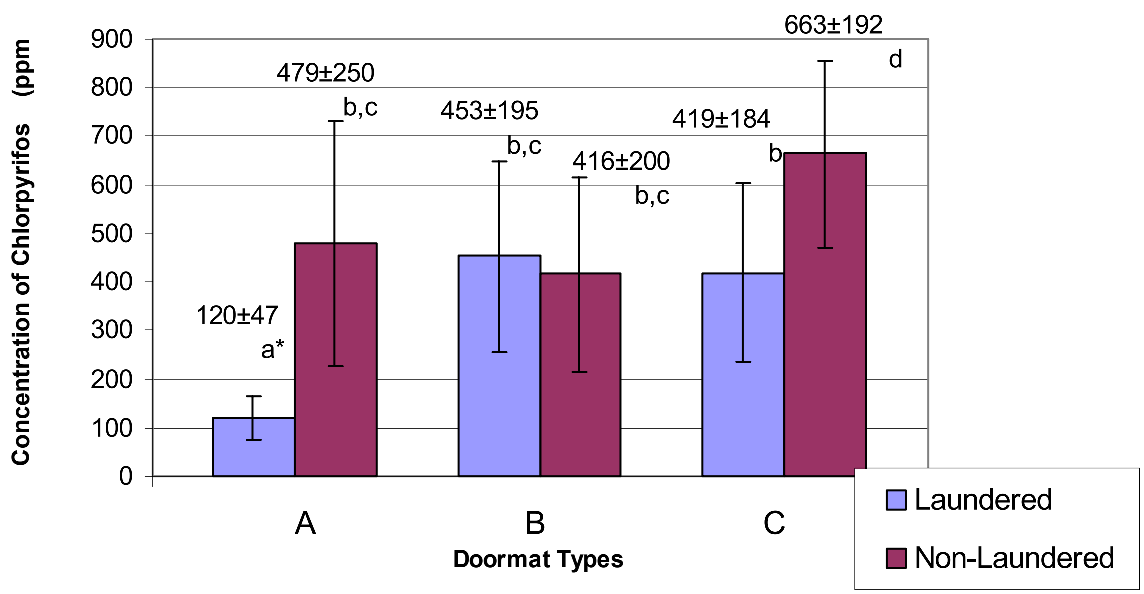


Figure 10: Concentration of chlorpyrifos extracted from laundered and non-laundered doormats

*Means sharing letters are not significantly different

Approximately 60% residue remained in the type B mats after laundering and 56% remained in the type C mats. The difference between non-laundered type A mats and laundered type B mats was not significant (*t*=0.29,p = 0.771). The difference between non-laundered type A mats and laundered type C mats was also not significant (*t*=0.67,p=0.503).

Discussion

Chlorpyrifos Load

The concentration of chlorpyrifos detected in the soil after treatment was 0.075 ± 0.009 mg/g. Since chlorpyrifos is a semi-volatile chemical, some of the applied pesticide may have been lost by partitioning into the air when the excess water was allowed to evaporate from the soil in a fume hood. This level of contamination is a more conservative estimate of the level of soil contamination possible in an area of pesticide mixing and loading. The intended level of contamination was 5 times higher than the level of contamination that could be expected in soil from a treated field, while the treated soil displayed a level of contamination at approximately 2 times higher than the level that could be expected in the field.

Dislodgeability Experiment

A high percentage of soil was dislodged from all of the doormats. The type C doormats trapped a statistically significant higher amount of soil compared to the A and B doormats. The lower amount of soil dislodged from doormat type C was likely due to its structure. A visual inspection of the vacuumed mats found soil particles within grouped looped fibers for mat types B and C. The soil particles remained near the top of the loops for type B mats. For type C mats, in addition to particles in looped fibers, the particles were present at the base of the mat. The type A mats had soil particles trapped in between yarns near the surface of the mat. The loop pile construction allowed for the trapping of soil particles within the looped yarns. Type A doormats had a flat woven structure with no gaps between yarns. Type B, a loop pile doormat, had a smaller pile height compared to type C and also had no gaps between yarns to allow soil particles to reach the mat base. Gaps in loop pile construction of type C would have allowed soil particles to fall below the surface of the fibers when a shoe was rubbed across the mat and a smaller amount of soil would be available on the surface of the fibers to track into the home.

The increased level of soil dislodged from type B doormats is influenced by the pile height. The shorter pile height for type B doormats (0.29 cm) compared to type C mats (4.0 cm and 0.50 cm) increased the ease of soil removal. A study examining the effect of carpet structure on the effectiveness of removing house dust mites by vacuuming determined pile height played a role in the increased removal of mites. Vacuuming was more effective at removing the mites trapped in the carpets with a short pile height compared to a tall pile height (Causer et al. 2004).

Doormats are recommended to reduce the transport of pesticides into the home on shoes and pets (Lewis et al. 1995; Clark 2004). Studies found doormats were partially effective in decreasing track-in (Nishioka et al. 1996; Nishioka et al. 1999). Heavy loading of soil may have resulted in the similar performance of the mat types. Curwin et al. (2005) found doormats did not reduce pesticide level in dust, which was suggested to have been due to high loading of pesticide and dust after a short time of use. The method of dislodging soil particles with the use of the HVS4 may have resulted in the similar levels dislodged. The vacuum would dislodge soil deep between the yarns in the mat, which would not be dislodged by foot traffic on the surface of the mat. This method of dislodging particles determined the total amount of soil available for track-in. With foot traffic, only a portion of this amount would be tracked into the home at one time.

The soil used for the experiment contained a percentage of water, as soil tracked in from farmers' fields would likely be moist. The presence of moisture could increase the transfer of pesticides. The estimates of pesticide tracked into the home in this study do not account for this phenomenon. Williams et al. (2002) treated nylon carpeting with pesticide and added water to the carpet at intervals to examine the transfer of residue over time as drying occurred. The level of pesticide transferable decreased over time as drying occurred, but increased to its initial level with the application of water (Williams et al. 2002).

Laundering Experiment

The amount of pesticide extracted from laundered type A and C doormats was statistically significant from non-laundered mats. Although the level of residue removed from the laundered type C doormat was significant, 44% of residues remained in the mats. A removal of less than 60% of the contaminant by laundering is not generally considered a successful laundering process. The high level of variability in the replicates of each treatment combination suggests that conclusions can not be drawn on the effectiveness of laundering. Some non-laundered samples had lower chlorpyrifos leveled detected than laundered samples suggesting the process of extracting chlorpyrifos from the mat samples is contributing a large amount of variability in the results.

In this study, the type A doormat showed the largest difference in the amount of pesticide removed. This is likely due in part to the different construction of the type A mat compared to the type B and C mats and the method used to launder the mats. The penetration of pesticides into fabric is influenced by the construction of the textile. The tightly woven type A mat did not allow for the trapping of soil particles in between the horizontal cotton yarns. The ability for the pesticide to be physically trapped within the mat affects the ability for laundering to remove pesticide residue. The spacing of the pile fibers in mats B and C prevented laundering from removing pesticides, which were able to penetrate the surface of the mat.

Type B and C mats were similar in construction and both were made of synthetic fibers. Laundering removed some of the pesticide residue from the type C mats, although there was a smaller reduction than with the type A mats. The laundering process did not significantly reduce the amount of pesticide in the type B mats. The fibers were positioned vertically in the doormat types B and C, whereas in doormat type A the woven yarns lay flat. This arrangement of fibers in mats B and C would have allowed soil particles to travel deep into the mat when the soil became mixed with the water during laundering, increasing the mobility of the soil. Both type B and C mats had a backing, which may have allowed soil particles to become trapped at the bottom of the fibers. Mats B and C, due to the backing, were less flexible than type A. Types B and C experienced less agitation in the launder-o-meter than type A, which may have contributed to the similar higher level of residue remaining in these mats. The more flexible type A mats were more thoroughly laundered. Synthetic fibers are non-absorbent, and therefore do not allow for detergent solutions to be readily absorbed, which may account for some of the higher level of pesticide remaining in the synthetic mats. Lorsban 4E, the formulation of chlorpyrifos chosen, is an emulsifiable concentrate, which is oil-based. The emulsifiable concentrate may have an affinity for the oleophilic fibers of nylon and polypropylene. Easter and DeJonge (1985) found azinphos-methyl as an emulsifiable concentrate proved difficult to remove from nylon fabric compared to other fabrics.

Large variability in the amount of pesticide removed by laundering may be influenced by how deeply the soil was embedded into the mat and soil being redeposited on the mat during the laundering process. The mats were not shaken to remove loose soil prior to laundering. Through the laundering process, soil and pesticide may have been deposited deeper into the mats. The water used in laundering can act as a carrier moving soil particles from one area on the mat to another. The soil applied to the mat would have become mixed with the water solution enabling the soil particles and pesticide to travel in between mat fibers. This process was likely present in mat types B and C where the vertical fibers and presence of a mat backing would have provided an area for the trapping of soil particles. Laughlin and Gold (1989) found pesticide in sections of fabric after laundering, which were not originally soiled.

The type of pesticide formulation used may affect results of the laundering process. Lorsban 4E, an oil-based pesticide, is hard to remove. Chlorpyrifos is stable in alkaline detergent. A study by Fitzgerald and Manley-Harris (2005) found that alkaline detergents were no more effective in removing chlorpyrifos from contaminated material than water alone.

Conclusions

The effectiveness of doormats in reducing the potential for pesticide contamination in the home due to track-in can not be determined from this study. The three types of doormats examined performed similarly in trapping soil, with each doormat type retaining approximately 30% of embedded soil. The similar performance may have been due to the method of dislodging the embedded soil, as the HVS4 would remove soil particles deep within the mat that foot traffic would not dislodge.

Although statistically significant differences were found in the effectiveness of laundering between the three mat types, the residue levels found in the replicates for each treatment combination were highly variable. Due to the variability, conclusions can not be drawn on the effectiveness of laundering. The large sources of variance were likely from the methods of embedding the soil, of laundering the mats, and of extracting the mats. Although the method of embedding the soil attempted to provide a consistent process, variations in the pressure of the foot press may have occurred when embedding the soil, resulting in some mats with more deeply embedded soil. During the laundering process soil on the surface of the mats may have been deposited deep into the mats. The extraction procedure did not remove all pesticide residues from the mats as 69% of residue remained in the non-laundered mats. After embedding the soil, no further treatment was applied to the non-laundered mats, thus the level of residues detected in the mat should be closer to the level applied.

Additional work should be completed to examine the dislodgeability of soil from doormats using a method that more closely simulates foot traffic. Determining the amount of soil tracked from an initial contaminated mat onto a second mat would provide an estimate of the level of soil brought into the home at one time. Further method testing should be done to develop a process to increase the agitation experienced by the mats during laundering. The efficiency of the extraction procedure needs refined. Factors such as solvent strength, extraction time, and number of extractions should be evaluated to develop a more consistent level of residue detection in the mats.

Also, the effectiveness of doormats in an actual setting should be examined. An evaluation of the amount of pesticide residue accumulated on doormats after a week of use and the percent of residue reduction after laundering would provide further information on the usefulness of doormats as a measure of mitigating contamination inside the home.

Appendices

Appendix 1. Soil analysis report

Report Number:
2004-R071-136
Account # 27032

A&L EASTERN AGRICULTURAL LABORATORIES, INC.

7621 Whitepine Road • Richmond, Virginia 23237 • (804) 743-9401
Fax No. (804) 271-6446 • Email: office@al-labs-eastern.com

Send To: NICK'S ORGANIC FARM LLC
NICK MARAVELL
8565 HORSESHOE LN
POTOMAC, MD 20854

Grower: NICK MARAVELL

Samples Submitted By:
NICK'S ORGANIC FARM LLC

SOIL ANALYSIS REPORT

Analytical Method:
Ammonium Acetate, Bray-P

Page: 4 Date Received: 03/10/2004 Date of Analysis: 03/11/2004 Date of Report: 03/12/2004

Sample Number	Sample Number	Organic Matter %	Organic Matter ENR lbs/A	Phosphorus Available ppm Rate	Phosphorus Reserve ppm Rate	Potassium K ppm Rate	Magnesium MG ppm Rate	Calcium CA ppm Rate	Sodium NA ppm Rate	pH Soil pH	pH Buffer Index	Acidity H meq/100g	CEC meq/100g
PNOR	10979	2.4	89 M	10 L	23 L	70 L	78 M	800 M		5.8	6.82	1.1	6.0
PEAS	10980	2.8	98 M	7 VL	25 L	55 L	68 M	850 H		6.0	6.84	0.9	5.9
PSOU	10981	2.1	84 M	5 VL	20 L	63 L	80 M	810 H		6.3	6.87	0.6	5.5
PWES	10982	2.2	85 M	5 VL	14 L	64 L	81 M	870 M		5.7	6.79	1.4	6.6
PNE	10983	2.6	94 M	5 VL	18 L	57 L	67 M	830 H		6.0	6.84	0.9	5.7

Sample Number	Percent Base Saturation K %	Mg %	Ca %	Na %	H %	Nitrate NO3-N ppm Rate	Sulfur SO4-S ppm Rate	Zinc Zn ppm Rate	Manganese Mn ppm Rate	Iron Fe ppm Rate	Copper Cu ppm Rate	Boron B ppm Rate	Soluble Salts ms/cm Rate	Chloride Cl ppm Rate	Aluminum Al ppm Rate
PNOR	3.0	10.9	67.1		19.0										
PEAS	2.4	9.7	72.5		15.4										
PSOU	3.0	12.2	74.3		10.6										
PWES	2.5	10.3	66.2		21.1										
PNE	2.5	9.7	72.3		15.4										

Values on this report represent the plant available nutrients in the soil.
Rating after each value: VL (Very Low), L (Low), M (Medium), H (High), VH (Very High).
ENR - Estimated Nitrogen Release. C.E.C. - Cation Exchange Capacity.

Explanation of symbols: % (percent), ppm (parts per million), lbs/A (pounds per acre), ms/cm (milli-mhos per centimeter), meq/100g (milli-equivalent per 100 grams).
Conversions: ppm x 2 = lbs/A, Soluble Salts ms/cm x 640 = ppm.

This report applies to the sample(s) tested. Samples are retained a maximum of thirty days after testing. Soil Analysis prepared by:
A & L EASTERN AGRICULTURAL LABORATORIES, INC.

by: C. Norman Jones

*** Soil samples obtained from PWES.**

Appendix Table 1. Dislodgeability experiment raw data: Amount of soil dislodged from type A doormats

Sample	High Level	Low Level	Zero Level
1	13.80	6.82	0.03
2	16.46	7.65	0.01
3	16.99	7.89	0.02
4	14.28	5.73	0.04
5	15.23	7.51	0.09

Mean ± standard deviation: high: 15.35 ± 1.37; low: 7.12 ± 0.87; zero level: 0.04 ± 0.03

Appendix Table 2. Dislodgeablility experiment raw data: Amount of soil dislodged from type B doormats

Sample	High Level	Low Level	Zero Level
1	15.04	7.00	0.06
2	16.75	8.16	0.05
3	15.97	7.41	0.05
4	14.81	7.18	0.00
5	15.02	7.00	0.06

Mean ± standard deviation: high: 15.52 ± 0.82; low: 7.35 ± 0.48; zero level: 0.04 ± 0.03

Appendix Table 3. Dislodgeablility experiment raw data: Amount of soil dislodged from type C doormats

Sample	High Level	Low Level	Zero Level
1	12.97	6.61	0.04
2	13.91	7.14	0.00
3	13.97	5.31	0.21
4	12.38	6.03	0.06
5	10.77	5.42	0.02

Mean ± standard deviation: high: 12.80 ± 1.32; low: 6.10 ± 0.78; zero level: 0.07 ± 0.08

Appendix Table 4. T-values and p-values for dislodgeablility experiment: high soil level

Mat Type	Mat Type	T-value (P-value)
A	B	-0.22 (0.8297)
A	C	3.38 (0.0055)
B	C	3.60 (0.0037)

Mat type main effect: $F_{(2,12)} = 8.14$, $p = 0.006$

Appendix Table 5. T-values and p-values for dislodgeablility experiment: low soil level

Mat Type	Mat Type	T-value (P-value)
A	B	-0.50 (0.6279)
A	C	2.20 (0.0480)
B	C	2.70 (0.0193)

Mat type main effect: $F_{(2,12)} = 4.13$, $p = 0.043$

Appendix Table 6. T-values and p-values for dislodgeablility experiment: no soil level

Mat Type	Mat Type	T-value (P-value)
A	B	-0.18 (0.8622)
A	C	-0.83 (0.4239)
B	C	-0.65 (0.5277)

Mat type main effect: $F_{(2,12)} = 0.38$, $p = 0.692$

Appendix Table 7. Laundering experiment raw data: Concentration of chlorpyrifos (ppm) extracted from type A doormats

Sample	Laundered	Non-laundered
1	102.49	823.29
2	100.61	836.28
3	126.88	679.52
4	222.57	560.81
5	188.87	640.80
6	124.43	165.29
7	82.385	318.23
8	101.43	394.27
9	58.735	211.08
10	90.935	160.14

Mean ± standard deviation: laundered: 120 ± 47; non-laundered: 479 ± 250

Appendix Table 8. Laundering experiment raw data: Concentration of chlorpyrifos (ppm) extracted from type B doormats

Sample	Laundered	Non-laundered
1	394.96	781.72
2	302.98	544.44
3	361.33	517.9
4	898.13	629.56
5	709.42	477.54
6	343.02	342.18
7	534.25	330.84
8	426.38	209.81
9	247.59	215.19
10	311.62	108.08

Mean ± standard deviation: laundered: 453 ± 195; non-laundered: 416 ± 200

Appendix Table 9. Laundering experiment raw data: Concentration of chlorpyrifos (ppm) extracted from type C doormats

Sample	Laundered	Non-laundered
1	299.60	730.64
2	454.54	930.63
3	535.46	750.24
4	580.01	823.83
5	713.89	864.66
6	585.41	672.83
7	61.274	661.88
8	356.81	480.41
9	231.45	369.96
10	371.50	345.75

Mean ± standard deviation: laundered: 419 ± 184; non-laundered: 663 ± 192

Appendix Table 10. T-values and p-values for laundering experiment

	Laundered Doormats			
Non-laundered Doormats		A	C	B
	A	4.04 (0.0002)	0.67 (0.5030)	0.29 (0.7711)
	C	-6.11 (<0.0001)	2.74 (0.0082)	-2.36 (0.0218)
	B	-3.33 (0.0016)	-0.04 (0.9708)	-0.42 (0.6771)

T-value (P-value)
Main effects: Mat type: $F_{(2,54)} = 7.41$, $p = 0.001$; Laundering: $F_{(1,54)} = 13.49$, $p<0.001$
Interaction: mat type and laundering: $F_{(2,54)} = 5.35$, $p = 0.008$

Appendix Table 11. T-values and p-values for laundering experiment

Mat Type	Mat Type	Laundered Doormats	Non-laundered Doormats
A	C	-3.36 (0.0014)	-2.07 (0.0432)
A	B	-3.74 (0.0004)	0.71 (0.4801)
C	B	0.38 (0.7040)	-2.78 (0.0074)

T-value (P-value)

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