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SOUTHWEST RESEARCH INST., SAN ANTONIO, TX

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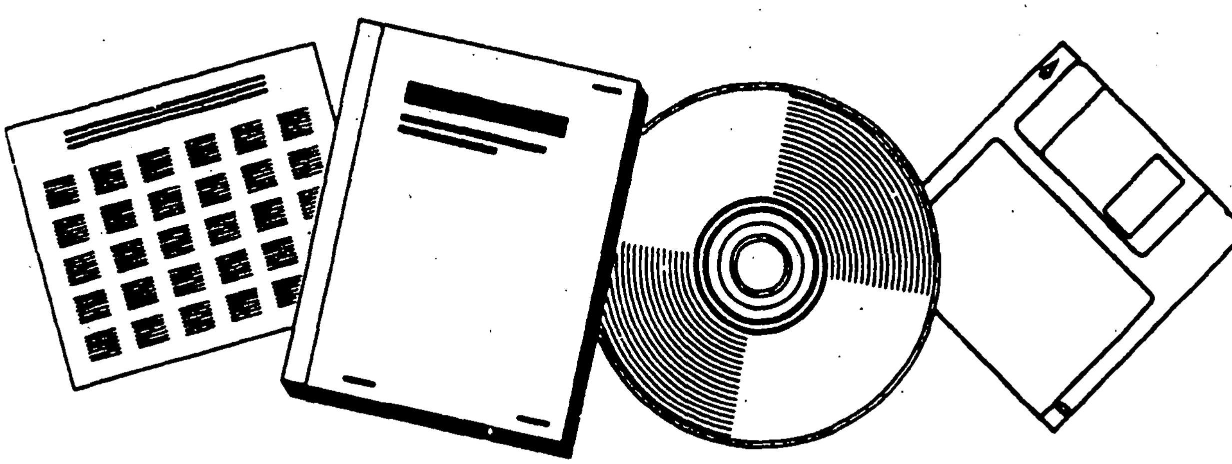

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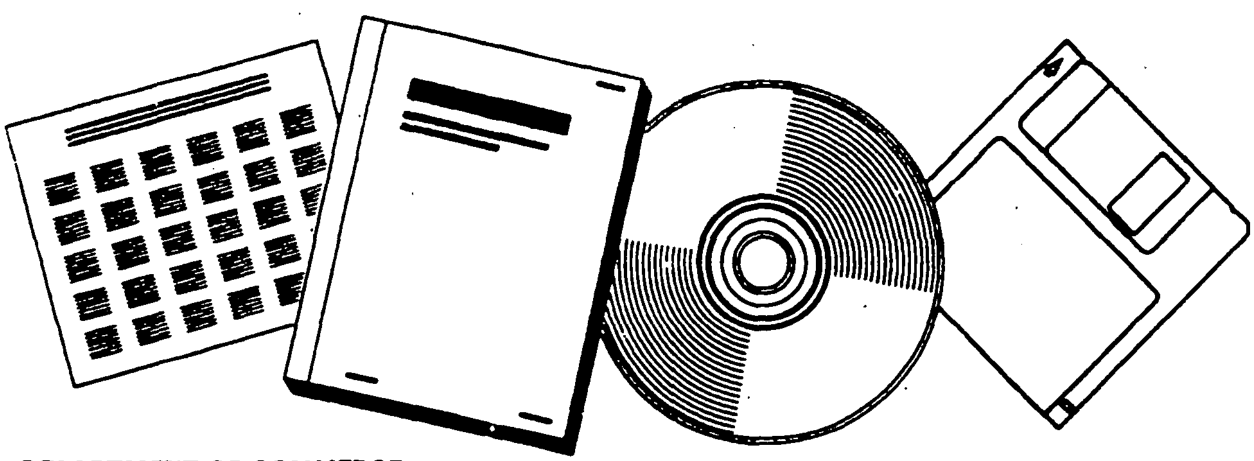

EPA/600/R-96/089
August 1996

COMPARISON OF METHODS TO DETERMINE DISLODGEABLE RESIDUE TRANSFER FROM FLOORS

FINAL REPORT

by

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Contract Number 68-DO-0007
Work Assignment No. 33
Battelle Subcontract No. 34501(2173)-2135
SwRI Project 01-5164

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U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

TECHNICAL REPORT DATA

1. REPORT NO. EPA/600/[illegible]	2.	PB96-196712
4. TITLE AND SUBTITLE **Comparison of Methods to Determine Dislodgeable Residue Transfer from Floors**		5. REPORT DATE August 1996 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) **David E. Camann, H.J. Harding, P. W. Geno, and S. R. Agrawal**		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS **Southwest Research Institute San Antonio, TX 78228-0510**		10. PROGRAM ELEMENT NO. **Issue 28/CC7E1A/E3156** 11. CONTRACT/GRANT NO. **68-DO-0007**
12. SPONSORING AGENCY NAME AND ADDRESS		13. TYPE OF REPORT AND PERIOD COVERED 14. SPONSORING AGENCY CODE **EPA/600/09**
15. SUPPLEMENTARY NOTES		

16. ABSTRACT

Three methods were evaluated for measurement of freshly-applied pesticide residues on carpeted and vinyl floors. Tests were conducted to determine the relative performance of the three methods for removal of dislodgeable residues and to compare them with human skin. The Dow drag sled and the Southwest Research Institute polyurethane foam (PUF) roller performed better than the California cloth roller. Moistening the sampling media increased the transfer by the drag sled and the PUF roller, but substantially increased measurement variability. An isopropanol handwipe method efficiently removed dried pesticide residues from the hands of volunteers (104% of chlorpyrifos, 92% of pyrethrin I).

Both the drag sled and the PUF roller were found to be acceptable dislodgeable residue methods on the basis of these studies. The transfer efficiency of the drag sled consistently exceeded the transfer efficiency of the PUF roller, which consistently exceeded the transfer efficiency of human hand presses. This relationship was observed for a variety of pesticides, loadings, application methods, and surfaces. The pliable polyurethane foam sampling surface of the PUF roller with its rolling action is likely to better simulate human skin in its transfer via contact with surfaces than is the denim cloth of the Dow sled with its drag action. Either mechanical method can be used to estimate dermal transfer of pesticide residues from recently treated floors. Round-robin testing of the drag sled and PUF roller by potential registrants under strict QA/QC guidance from EPA is recommended.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/ OPEN ENDED TERMS	c. COSATI
18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES 122
	20. SECURITY CLASS *(This Page)*	22. PRICE

Disclaimer

The information in this document has been funded by the United States Environmental Protection Agency under (Contract Number 68-DO-0007) to Battelle and Subcontract No. 34501(2173)-2135 to Southwest Research Institute. It has been subjected to the Agency's peer and administrative review, and it has been approved for publication as an EPA document. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Foreword

The National Exposure Research Laboratory, Research Triangle Park, North Carolina, conducts intramural and extramural research in the chemical, physical, and biological sciences. This research is intended to characterize and quantify environmental pollutant levels and the resulting exposures of humans and ecosystems; to develop and validate models to predict changes in pollutant levels; to determine source-receptor relationships affecting ambient air quality ar d pollutant exposures; and to solve scientific problems relating to EPA's mission through long-term investigations in the areas of environmental measurement methods, quality assurance, biomarkers, spatial statistics, exposure assessment, and modeling. The Laboratory provides support to Program and Regional Offices and state and local groups in the form of technical advice, methods research and development, quality assurance, field monitoring, instrument development, and modeling for quantitative risk assessment and regulation. The Laboratory also cc¨ects, organizes, manages, and distributes data on environmental quality, human and ecosystem exposures, and trends for the Program and Regional offices, the Office of Research and Development, the scientific community, and the public.

Human exposure to pesticides after application in the home is an area of concern to EPA because of the toxicity of these chemicals. Dermal exposure through direct skin contact with treated surfaces may be important, especially for toddlers, but is poorly understood, because sampling methods have not been validated. The work described in this report evaluates and validates mechanical methods for determining the amount of pesticide residue on floors which transfers to the hands through direct contact.

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Abstract

Comparisons were made of transfer of formulated pesticide residues from treated carpets and vinyl flooring by three dislodgeable residue methods and by human skin. The Dow drag sled and the Southwest Research Institute polyurethane foam (PUF) roller performed better than the California cloth roller. Moistening the sampling media increased the transfer by the drag sled and the PUF roller, but substantially increased measurement variability. An isopropanol handwipe method efficiently removed dried pesticide residues from the hands of volunteers (104% of chlorpyrifos, 92% of pyrethrin I).

Both the drag sled and the PUF roller were found to be acceptable dislodgeable residue methods on the basis of these studies. The transfer efficiency of the drag sled consistently exceeded the transfer efficiency of the PUF roller, which consistently exceeded the transfer efficiency of human hand presses. This relationship was observed for a variety of pesticides, loadings, application methods, and surfaces. The pliable polyurethane foam sampling surface of the PUF roller with its rolling action is likely to better simulate human skin in its transfer via contact with surfaces than is the denim cloth of the Dow sled with its drag action. Either mechanical method can be used to estimate dermal transfer of pesticide residues from recently treated floors. Round-robin testing of the drag sled and PUF roller by potential registrants under strict QA/QC guidance from EPA is recommended. The work reported herein was performed by Southwest Research Institute under U.S. Environmental Protection Agency Contract No. 68-DO-0007 to Battelle Memorial Institute.

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Section 1
Introduction

Dermal transfer through contact with residues of pesticides applied to floors and subsequent skin absorption or ingestion through hand-to-mouth activity are routes of human exposure which need better evaluation, especially for young children. The Dow drag sled (Vaccaro and Cranston, 1990), the California cloth roller (Ross et al., 1991), and the Southwest Research Institute (SwRI) polyurethane foam (PUF) roller (Hsu et al., 1990) (Patent No. 5,243,865) are dislodgeable residue sampling methods which have recently been developed to estimate the transfer of a chemical from a contaminated surface to the skin. This work assignment compared these methods to provide some of the data to determine which provides the most accurate, reproducible, economical, and facile performance. Precision and bias relative to human skin pick-up were also investigated. The goal was to obtain data from which standardized methods can be established for use by registrants and researchers.

The first phase of this work assignment compared both the rate (ng/cm^2 of carpet contacted) and the variability of transfer from carpet after broadcast spray application of a chlorpyrifos formulation by each of these methods as currently employed by the developer. Three experiments were performed:

Exp. 1. Transfer comparison of the three methods using dry sampling media on new plush cut-pile nylon carpet.

Exp. 2. Transfer comparison of the three methods using dry sampling media on new level-loop polypropylene carpet.

Exp. 3. Transfer comparison of the better two methods using both dry and moist sampling media on new plush cut-pile nylon carpet.

In the second phase of the work assignment, transfers determined by human skin contact were compared to transfers obtained by the better-performing mechanical methods (i.e., the drag sled and the PUF roller). Experiments 4 through 8 were performed:

Exp. 4. Determination of the wipe removal efficiency by an isopropanol handwipe method of two pesticides (chlorpyrifos and pyrethrins) that have been applied to the skin of the hands.

Exp. 5. Experiments 5A through 5E investigated the effects of sampling variables on the amount and variability of dislodgeable residue transfer of formulated chlorpyrifos from plush carpet when using the drag sled and PUF roller. The sampling variables which were evaluated included traverse distance, number of repeat passes over the same section of carpet, speed, and transfer pressure.

Exp. 6. Comparison of the transfers of formulated chlorpyrifos, pyrethrins, piperonyl butoxide, and methoprene residues from plush nylon carpet obtained by the drag sled, the PUF roller, and human hand presses.

Exp. 7. Comparison of the transfers of formulated chlorpyrifos, pyrethrins, and piperonyl butoxide residues from sheet vinyl flooring obtained by the drag sled, the PUF roller, and human hand presses.

Exp. 8. Evaluation of the effect of air/carpet temperature on the transfer of fresh and aged residues of formulated chlorpyrifos, pyrethrins, and piperonyl butoxide residues by the drag sled and the PUF roller from plush nylon carpet.

Section 2
Conclusions

1. Transfers as currently performed by the developer were largest for the California cloth roller, intermediate for the drag sled, and smallest for the PUF roller when using dry sampling media on two types of carpet.

2. The California cloth roller is less practical and more variable than the drag sled or PUF roller methods.

3. Transfers with moist media are larger, but substantially more variable, than transfers with dry media, for both the PUF roller and the drag sled.

4. An isopropanol hand wipe method efficiently removed dry pesticide residues from the hands of two volunteer subjects within the first minute after their transfer from aluminum foil to the hand. Wipe removal efficiency was determined by mass balance after accounting for extraction and elution efficiency. The mean wipe removal efficiencies were 104% (s=11%, n=12) for formulated chlorpyrifos, and 92% (s=28%, n=12) for pyrethrin I (formulation fortified with analytical standard).

5. Both the drag sled and the PUF roller transferred an amount of formulated chlorpyrifos residue from plush carpet which was generally proportional to the length of carpet traversed. An essentially constant amount of chlorpyrifos appeared to transfer to the PUF roller on each of the first 20 passes over a 1 m strip of plush carpet.

6. Increasing the pressure applied to chlorpyrifos-treated plush carpet through the sampling medium had little effect on chlorpyrifos transfer by the drag sled, but produced a nearly proportional increase in transfer by the PUF roller.

7. As the carpet temperature increases, the drag sled and PUF roller both transfer slightly larger amounts of fresh and aged residues from plush carpet.

8. The transfer efficiency of formulated pesticide residues from treated carpets and vinyl flooring was consistently highest for the drag sled, intermediate for the PUF roller, and lowest for human skin.

9. The flooring material and application method and/or formulation had major effects on transfer, but the specific active ingredient had virtually no effect.

10. The observed mean ± standard deviation of the multiplier of hand press transfers obtained by the mechanical methods was 7.4 ± 2.8 for the drag sled and 3.3 ± 2.1 for the PUF roller. Either mechanical method can be used to estimate dermal transfer of pesticide residues from recently treated floors.

Section 3
Recommendations

1. Both the drag sled and the PUF roller were found to be acceptable dislodgeable residue methods on the basis of this study.

2. Round-robin testing of the drag sled and PUF roller is recommended under strict QA/QC guidance from EPA.

3. Dermal transfer of pesticide residues can be estimated from transfer by the drag sled or PUF roller. Ratios which appear to apply to measurements on recently treated floors were obtained in this study.

Section 4
Materials and Methods

4.1 Facility Preparation

All experiments were performed on the SwRI campus. All except Experiment 4 were performed in an empty room (9 ft x 15 ft) in a 42 ft x 10 ft 3-room trailer, and in half of the adjacent empty room for Experiments 1 and 2. Virgin flooring was installed prior to some experiments: a DuPont® Stainmaster[CM] 100% nylon continuous filament textured plush cut-pile carpet and padding prior to Experiment 1, a Shaw Mark® Provider 26 polypropylene tufted textured level-loop carpet and padding prior to Experiment 2, an Evans and Black® Scotchgard[CM] 100% nylon Saxony plush cut-pile carpet and padding prior to Experiment 3, and Armstrong Explorer Solarian No. 66510 sheet vinyl installed on ¼ in. wood underlayment prior to Experiment 7. The plush cut-pile nylon carpet used for Experiment 3 was reused for succeeding experiments. It was cleaned using a commercial water extraction system prior to the conduct of Experiments 5A, 5B, 5C1, 5C2, 5E1, 5E2, 5D, 6A, 6B, and 8B. Each cleaning consisted of application of a spot cleaner to remove marks, extraction using a chemical carpet cleaner, rinsing with clean water, and drying for 48 hours with rapid air ventilation. Experiment 4 was performed in three extraction laboratories.

4.2 Dislodgeable Residue Methods

In Experiments 1, 2, and 3, the dislodgeable residue methods were performed as employed by their developers. Relevant characteristics of these dislodgeable residue methods are summarized and contrasted in Table 1.

The California cloth roller was constructed and the method performed as described by Ross et al. (1991). A soap-washed and precleaned dry 17 in. x 17 in. cloth of percale bed sheet was placed on the carpet and covered with a sheet of plastic. A 2 ft long by 4 in. diameter sewer pipe, filled with 25 pounds of steel shot ballast and wrapped in a sheet of high density PUF, was rolled forward and backward over the plastic/cloth/carpet sandwich ten times (Figure 1). After the 20 passes, the percale cloth was picked up and analyzed.

The drag sled method was performed using the initial configuration described by Vaccaro and Cranston (1990). Briefly, a precleaned dry 4 in. x 4 in. denim weave cloth supplied by B. Shurdut, Dow Chemical Company, was attached beneath foil under a 3 in. x 3 in. plywood block and an 8-lb weight mounted (Figure 2). The sled was dragged once over a 3 in. x 4 ft carpet strip at 6-8 cm/s. After the single pass, the denim cloth was removed for analysis.

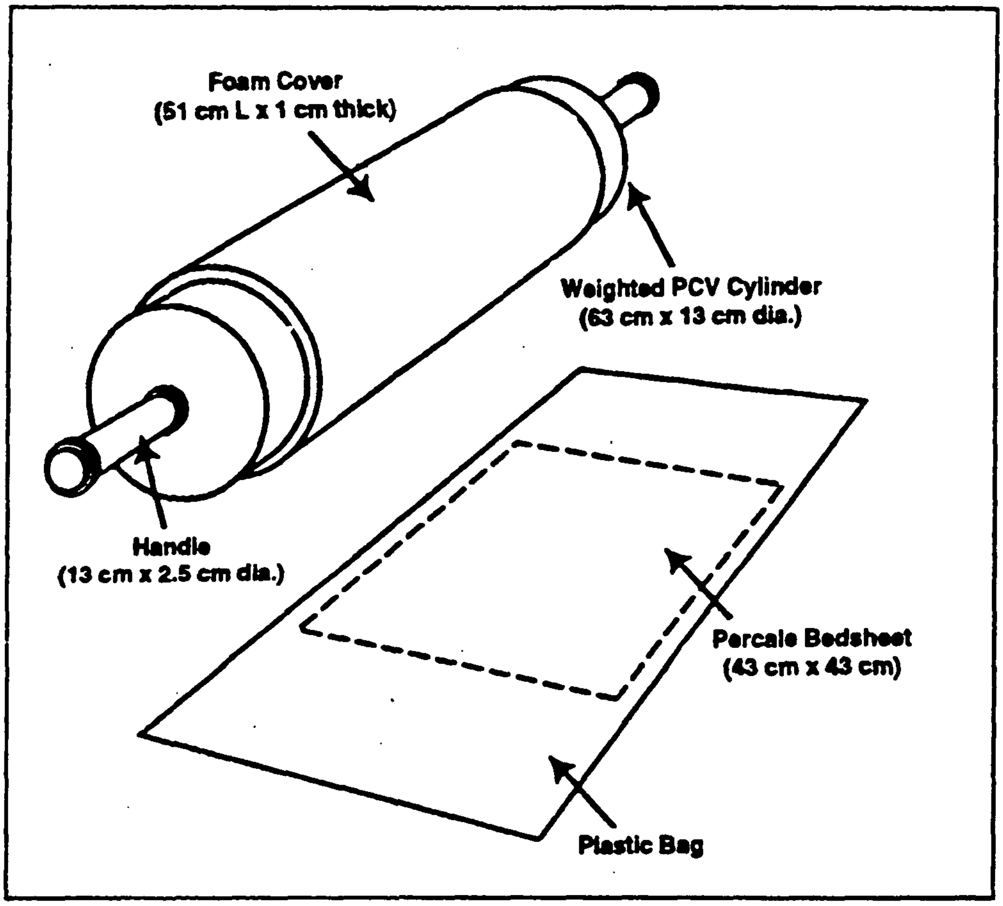


Figure 1. California cloth roller.

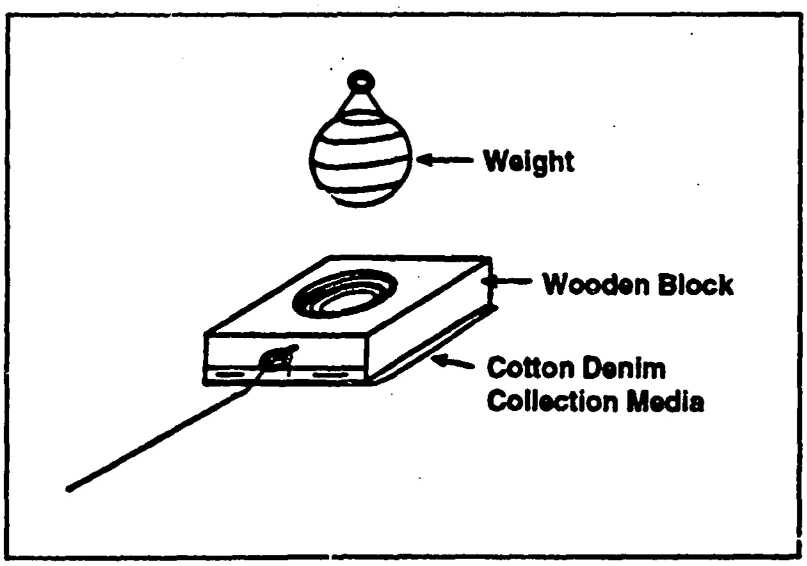


Figure 2. Dow drag sled

The original PUF roller sampler (Hsu et al., 1990) was used for Experiments 1 and 2. A precleaned dry PUF ring (3 in. length, 3.5 in. OD, 1.62 in. ID) was secured on the 8 in. length x 2 in. OD cylindrical 7.2 lb stainless steel roller. The new (October 1992) model of the PUF roller sampler was constructed and used for Experiment 3 and later experiments. A precleaned dry PUF ring was secured on the 3 in. length x 1.75 in. OD cylindrical 0.37 kg aluminum roller (Figure 3). The PUF roller was rolled once over a 3 in. x 1.0 m carpet strip at 10 cm s once in both directions. After the two passes, the PUF ring was slit and removed from the roller for analysis.

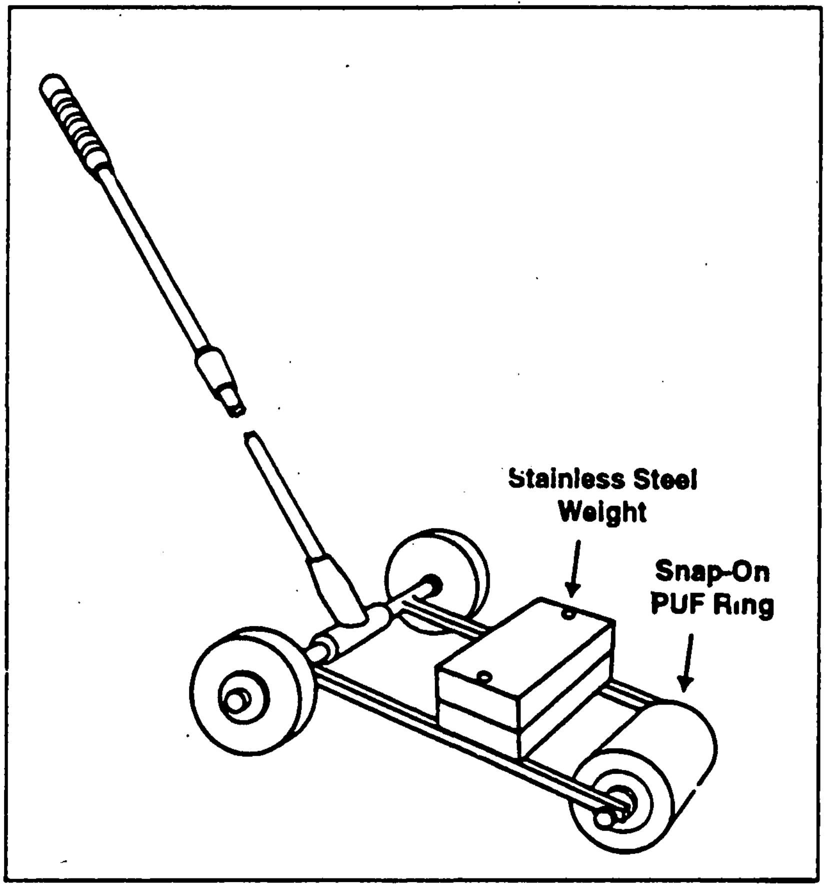


Figure 3. PUF roller sampling instrument (1992 model).

In Experiment 3, PUF rings and denim cloth were used which had been moistened with deionized water. A precleaned PUF ring was uniformly moistened with 5.0 ± 0.1 g of water in the laboratory by spraying the ring surface with an atomizer, compressing with a squeeze tool to obtain uniform water distribution, weighing and sealing in a steel canister until use. The sampling surface of the denim cloth was moistened with 0.5 ± 0.1 g of water from the atomizer and weighed just prior to mounting under the drag sled. When moistened at these levels, the PUF ring and denim cloth were observed to produce equivalent moisture trails at method pressure on a glass surface.

Later experiments involved only the drag sled and the PUF roller dislodgeable residue methods. To allow more direct cross-comparisons of these methods with each other and the human hand press, a single pass over a floor traverse distance of 1.0 m was used as a standard floor sampling technique for both methods. Relevant characteristics of the methods as employed in Experiment 7 are presented in Table 2.

4.3 Hand Press and Wipe Methods

In Experiments 6B and 7, a set of ten presses of the treated flooring was made with each hand by three subjects on three days in a reproducible manner. Prior to each daily pair of hand presses, each subject thoroughly washed his hands with soap and water. The subject was cautioned to avoid touching any surfaces during the hand press and wipe sequence. The subject then placed a disposable nitrile glove over the non-test hand. The second hand was gloved to prevent contamination while performing the press and wipe procedure on the first hand and to prevent the isopropanol from drying out the skin of the second hand prior to the hand press (avoiding an abnormal skin condition that could affect hand press transfer efficiency). A cardstock template was placed over the designated area for floor sampling to expose a 3 in. (7.6 cm) x 25 in. (63.5 cm) treated strip. While kneeling on a cardboard mat, each subject performed a series of ten presses of the palm of the test hand to adjacent sections of flooring exposed by the template at a pressure of ca. 1.0 psi for 1 sec each with fingers held off of the surface. An isopropanol handwipe of the hand was performed as described by Camann et al. (1995) in a clean area in another building. After washing both hands with soap and water, the glove was removed from the second test hand and a clean glove placed over the second non-test hand. The press and wipe procedures described above were then repeated using the second hand.

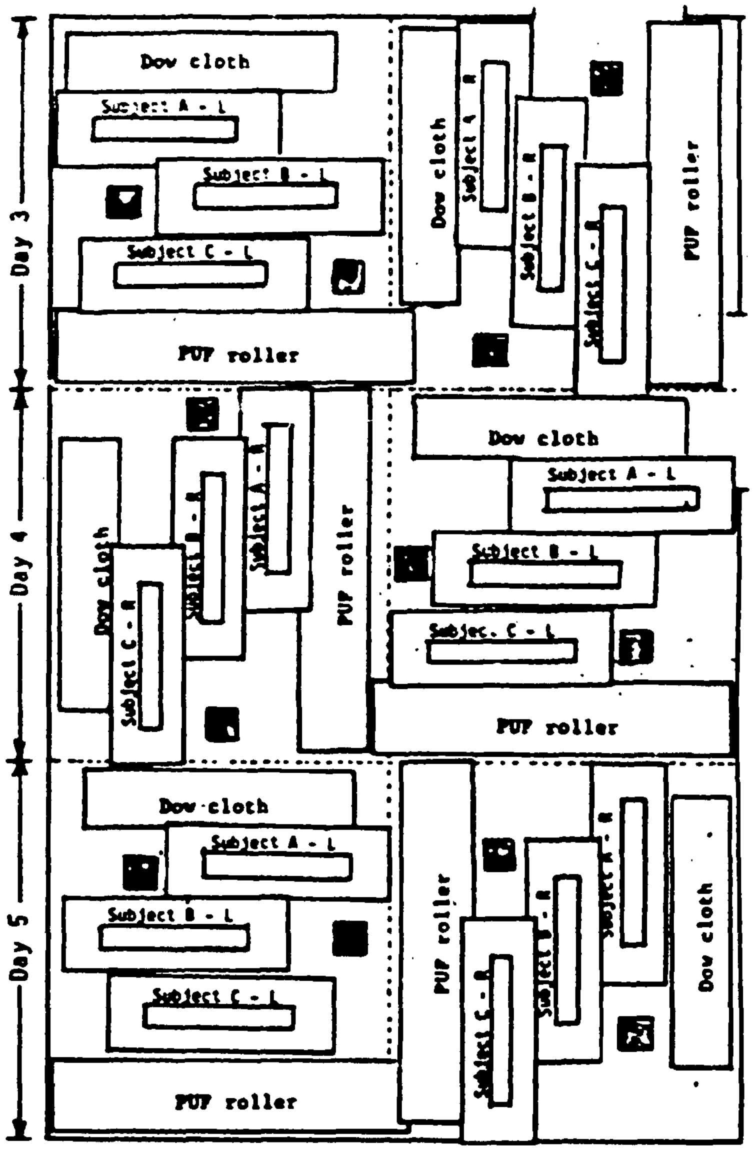
The handwipe utilized two Sof-Wick® 4 in. x 4 in. 6-ply dressing sponges which had been pre-cleaned prior to use. Each sponge was laced with 10 mL of Optima grade isopropanol. The subject was asked to perform a general wipe of each hand with the first sponge. The second sponge was used to wipe around and between each digit. Both sponges were then placed in a single container and an additional 50 mL of isopropanol was added. The subject performed all direct handling of the sponges from preparation to placement in the sample container, although handling via forceps was also permitted. Immediately following each handwipe procedure, the subject thoroughly washed his hands to remove any remaining pesticides residues.

4.4 Pesticide Application

Application of the formulated pesticide to test flooring was conducted by a licensed pest control applicator according to label instructions for flea control treatment. The active ingredients of the formulations applied for each experiment are listed in Table 3. Each application was accomplished in 2-3 min.

Chlorpyrifos was broadcast applied in the early experiments. The formulated product, Dursban® L.O. (EPA Registration No. 464-571) which contains 41.5% chlorpyrifos (O,O-diethyl O-[3,5,6-trichloro-2-pyridyl]phosphorothioate), was applied approximately 40 cm above the carpet as a 0.50% aqueous spray (40 mL/3.785 L water) at a rate of 1 gal/1600 ft^2 with a hand-held fan broadcast nozzle attached to an air pressurized tank.

For Experiments 6 and 7, which involved human hand presses of the treated flooring, a pesticide formulated mixture was applied according to label instructions to control a light infestation of fleas. A chlorpyrifos/pyrethrins/piperonyl butoxide formulated mixture was broadcast applied for Experiments 6A, 8B, and 7. The formulated emulsifiable concentrate products, Dursban® L.O. (EPA Registration No. 62719-55), which contains 41.5% chlorpyrifos (O,O-diethyl O-[3,5,6-trichloro-2-pyridyl]phosphorothioate), and Kicker® (EPA Registration No. 4816-707AA), which contains 6.0% pyrethrins and 60.0% technical piperonyl butoxide were tank mixed at 2/3 fl. oz. (20 mL) Dursban® L.O. and 0.5 fl. oz. (15 mL) Kicker® per gallon of water to yield 0.25% chlorpyrifos, 0.025% pyrethrins, and 0.25% piperonyl butoxide in the aqueous spray. The mixture was applied approximately 40 cm above the floor at a rate of 1 gallon of diluted mixture per 1600 square feet with



Sample Layout for Experiment 7: Hand Press Collection Efficiency on Vinyl Sheet Flooring

- Day 3 - North block
  - 4 deposition coupons
  - 2 PUF roller samples (with. acetone)
  - 2 Dow cloth samples (with. acetone)
  - 6 hand presses (both hands of subjects A, B, & C)
- Day 4 - Center block
  - 4 deposition coupons
  - 2 PUF roller samples (with. acetone)
  - 2 Dow cloth samples (with. acetone)
  - 6 hand presses (both hands of subjects A, B, & C)
- Day 5 - South block
  - 4 deposition coupons
  - 2 PUF roller samples (with. acetone)
  - 2 Dow cloth samples (with. acetone)
  - 6 hand presses (both hands of subjects A, B, & C)

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Figure 4. Sampling layout for Experiment 7.

a hand-held fan broadcast nozzle attached to an air pressurized tank. For Experiment 6B, Vet-Kem® Siphotrol® premise spray (EPA Registration No. 2724-338-11785), which contains 0.015% methoprene, 0.20% pyrethrins, and 1.0% technical piperonyl butoxide, was applied from the aerosol can using a sweeping motion to supplement the residues left on the carpet after Experiment 6A.

The trailer was ventilated for 2 hr immediately after application. All windows were opened and window air conditioning units were operated in fresh return air mode. During the first 30 min and last 15 min of the ventilation period, both doors were opened and a box fan was operated outside the test room doorway to allow maximum cross ventilation. For experiments performed in warm weather, air conditioner units were returned to the usual recirculated air mode just prior to sampling and remained on throughout the sampling period of the experiment.

4.5 Sampling Designs for Experiments on Floors

The designs to determine comparative method transfers in the floor sampling experiments employed many common design and QA/QC elements. Adjacent samples using each compared dislodgeable residue and hand transfer method and a deposition coupon were collected sequentially within a rectangular block of treated carpet or vinyl. Six replicate blocks were sampled in most experiments, although fewer were employed when there was insufficient available treated surface. The block design of the sample layout for Experiment 7 is illustrated in Figure 4.

Deposition coupons, consisting of absorbent alpha-cellulose pads (4 in. x 4 in.) backed with aluminum foil were placed on the carpet (or teflon sheets on vinyl flooring) prior to the pesticide application and picked up before the adjacent dislodgeable residue/hand samples from the block were collected. Residues measured on the coupon (or coupon set) gave an estimate of the surface loading of residue remaining on adjacent carpeting/vinyl during sampling in the block.

Field blanks of each method were obtained by sampling prior to the application to assess contamination potential during sampling and handling. Deposition coupon(s) were placed at the designated locations in each sampling block shortly before the application commenced. Field samples were collected in the first block upon label allowed re-entry, i.e., when the carpet was dry (which was operationally defined as 2 hours after application, but checked by hand contact). The dislodgeable residue samples of a block were collected from specific randomized locations in the block after the deposition coupon(s) were picked up. All samples were collected in one block before proceeding to the next block. Spikes of the precleaned dislodgeable residue media and of a deposition coupon were made both before and after the set of replicate block samples were collected; these field spikes were used to assess and potentially adjust for losses during transport, storage, and extraction.

The design used for Experiment 1 on new plush cut-pile carpet and for Experiment 2 on new level-loop polypropylene carpet is presented in Table 4. The design used to compare transfers with dry and moistened media is presented in Table 5. The designs used to evaluate the effects on transfer of PUF roller sampling variables in Experiments 5A, 5B, and 5C and of drag sled sampling variables in Experiments 5D and 5E are given in Tables 6-10. Tables 11 and 12 present the designs employed in Experiments 6 and 7 to compare transfers of applied pesticides from plush carpet and from sheet vinyl obtained by the drag sled, PUF roller, and human hand presses. The designs used in Experiments 8A and 8B to investigate the effect of temperature on transfers of aged and fresh pesticide residues by the drag sled and PUF roller are presented in Tables 13 and 14.

4.6 Sampling Design for Experiment 4

4.6.1 Task 4A: Determination of Aluminum Foil Elution Efficiency

In order to determine the efficiency of removal of chlorpyrifos and natural pyrethrins from aluminum foil squares, seven foils were spiked with 250 µL of the diluted formulated mixture. An additional seven foils were spiked with 25 µL of the formulated mixture. The factor of ten difference in spike levels was to determine if aluminum foil elution efficiency is independent of the amount of pesticide spiked. Two additional foils were extracted without spiking to serve as control blanks. In order to verify the level of the pesticides in the spike solution, two 300 mL portions of 1:1 ether:hexane were each spiked with 250 µL and with 25 µL of the diluted formulated mixture.

4.6.2 Task 4B: Determination of Handwipe Extraction Efficiency

The efficiency of the extraction method for removal of the target pesticides from the handwipes was evaluated by spiking seven moistened, precleaned handwipes with 250 µL of the diluted formulated mixture. An additional seven wipes were spiked with 25 µL of the diluted formulated mixture. The factor of ten difference in spike levels was to determine if the handwipe extraction efficiency is independent of the amount of pesticide spiked. Two handwipes were extracted without spiking and served as control blanks, and two aliquots of isopropanol were each spiked with 250 µL and with 25 µL of the diluted formulated mixture.

4.6.3 Task 4C: Determination of Handwipe Removal Efficiency

Handwipe removal efficiency experiments were performed using two human subject volunteers on each of three days. On each day prior to sampling, the subject's hands were inspected for rashes, abrasions or cuts in the skin. When any such sores existed, the experiment was postponed until the hand healed. On Days 1, 2, and 3, five aluminum foil squares were spiked with 50 µL of the diluted formulated mixture as described above, one aluminum foil square was spiked with 25 µL of the diluted formulated product, and one foil square served as a control blank. Hand presses were performed on four of the 50 µL spiked foil squares, corresponding to each hand of each of the two subjects. A disposable nitrile glove was placed over the non-test hand for the press and wipe of the test hand. The order in which the two hands were sampled was alternated on the three days. The double isopropanol handwipe procedure described above was initiated immediately (within 1 min) following each hand press. On each day, one additional handwipe (i.e., isopropanol-moistened pair of Sof-Wick® sponges) was spiked directly with 50 µL of the diluted formulated mixture, one handwipe was spiked with 25 µL of the diluted formulated mixture and one handwipe served as a control blank. In order to verify the level of the pesticides in the spike solution, one 300 mL portion of 1:1 ether:hexane each was spiked with 50 µL and with 25 µL of the diluted formulated mixture and one portion served as an extraction blank. A summary of samples for the three described tasks is given in Table 15.

4.7 Protocols and Informed Consent

A protocol was written to describe each planned experiment in detail and was submitted to the project officer prior to conduct of the experiment. Estimates were made and documented in each protocol of the expected dermal exposure of the volunteer human subjects who participated in Experiments 4, 6, and 7. Prior to the conduct of each of these experiments, their protocols and consent forms were approved by the Institutional Review Board of the University of Texas Health Science Center at San Antonio, and informed consent of each volunteer subject was obtained. The protocols for Experiments 4 and 7 are given in Appendices A and B, respectively.

4.8 Sample Analysis

Dislodgeable residue samples were Soxhlet-extracted with 6% ethyl ether/94% hexane; extraction commenced within 24 hours after sampling. The pair of deposition coupons from a block were usually combined and rinsed with 6% ether-hexane as a single sample. Isopropanol-saturated handwipes were shake extracted with 1:1 diethyl ether:hexane (Camann et al., 1995).

Extracts from Experiments 1, 2, 3, and 5 were analyzed for chlorpyrifos by GC/ECD on two dissimilar columns and quantitated from the DB-5 column results. Extracts from Experiments 4, 6, 7, and 8 were analyzed for chlorpyrifos, methoprene, piperonyl butoxide and/or pyrethrin I on a Fisons MD-800 GC/MS operating in selected ion monitoring mode.

4.9 Data Adjustment

Crude results (µg/sample) from each field sample were adjusted for contamination by subtracting the field blank result as appropriate. Extraction efficiency was evaluated by maintaining a control chart of the field spike recoveries for each matrix. Since field spike recoveries were generally close to 100% (see Results), the reported data have not been adjusted for extraction inefficiency, except as specifically noted. This result was divided by the sampled carpet area (see Tables 1 and 2) to determine the measured transfer rate (ng/cm^2 of carpet contacted) for dislodgeable residue samples and the measured surface loading (ng/cm^2) for coupon samples.

Section 5
Results and Discussion

5.1 Conduct of Experiments

The experiments were conducted over a 13-month period from August 1992 through August 1993. The sampling dates and times are given in Table 16. The temperature and relative humidity of the trailer room air were monitored during each sampling period beginning with Experiment 5; mean levels are reported in Table 16. The mean carpet temperature during each transfer sampling period of Experiments 7 and 8 is also presented in Table 16.

5.2 Data Quality

5.2.1 Field Blanks

Field blanks were obtained with the cloth roller, drag sled, and PUF roller before pesticide applications. The low amounts obtained on these field blanks in comparison with measurements after application established that transfers from the floor were elevated substantially by each application.

The pesticide amounts recovered on each of the hand press/isopropanol handwipe field blank samples in Experiments 4, 6,and 7 are presented in Table 17, along with the isopropanol gauze laboratory blank results. A field blank consisted of a hand press by a subject onto the test surface or a superimposed clean surface in the same room where the hand press samples were subsequently collected, followed by the double isopropanol wipe of the hand after the subjects walked to a clean area in another building. The field blank hand press consisted of a single press/rub of clean aluminum foil in Experiment 4C, a single press through a cardstock template onto 48 cm^2 of a commercially-cleaned reused plush carpet in Experiment 6A, and ten adjacent hand presses onto a clean cardstock strip placed over the test flooring in Experiments 6B and 7. Chlorpyrifos was recovered in 41 of the 42 hand press field blanks, in amounts ranging from 0.10 to 0.88 µg/sample. Piperonyl butoxide was detected in 2 of 34 hand press field blanks, but at levels (0.06 µg and 0.03 µg) similar to those in solvent blanks. Pyrethrin I and methoprene were not detected in the hand press field blanks. Neither chlorpyrifos nor pyrethrin I were detected in the three isopropanol gauze lab blanks analyzed in Experiment 4C, which were the only lab blanks performed.

The source of the chlorpyrifos contamination seen in the hand press field blanks is unclear. Chlorpyrifos is used extensively in the southern United States for indoor and outdoor insect control. The chlorpyrifos levels were similar on both hands of all subjects on each day that hand press field blanks were obtained. The mean chlorpyrifos blank levels collected on Day 2 of Experiment 7 and on Day 0A of Experiment 6A were higher than on the other days. The subjects always performed their presses of the same hand in the sequence A, B, and C. Subject A had elevated chlorpyrifos levels in the first (right) hand press blank he performed on Day 2 of Experiment 4C, on Day 0A of Experiment 6A, and on Day 2 of Experiment 7. Through monthly chlorpyrifos dip treatments of his dogs, and by petting them before work, Subject A is likely to have had some chlorpyrifos residue on his hands each morning. However, he washed his hands with soap and water several times before the day's field blank sampling commenced. Subject A carried the bar of Ivory® soap to the sink where the subjects used it to wash their hands before and after each hand press. It is possible that chlorpyrifos residues were transferred to, and from, the faucet handle or the soap bar during hand washing by the sampling team or subjects. Another possibility is that these hand blanks reflect ambient chlorpyrifos residues which were previously transferred to the skin. Chlorpyrifos in fats and oils which are deeply embedded in the skin may not be removed by washing with soap and water. However, the more efficient double isopropanol handwipe procedure may remove the fats and oils containing the chlorpyrifos, to yield the residues seen in the hand press field blanks.

5.2.2 Field Spikes

Series of field spikes were obtained across the eight experiments for alpha-cellulose deposition coupons, denim drag cloths, PUF rings, isopropanol-moistened Sof-Wick® gauze handwipes, and aluminum foil squares. The field spike recoveries of chlorpyrifos, methoprene, piperonyl butoxide, and pyrethrin I for each of these series are presented by matrix in Tables 18 through 22.

Chlorpyrifos recoveries from alpha-cellulose coupons, drag cloths, PUF rings, and aluminum foil were essentially quantitative, with mean field spike recoveries near 100%. Chlorpyrifos recovery from isopropanol-moistened gauze was slightly lower, averaging 86%. Mean recoveries of methoprene, piperonyl butoxide, and pyrethrin I from these media were generally within one standard deviation of 100%, although recoveries of piperonyl butoxide from alpha-cellulose and of methoprene from isopropanol-moistened gauze were lower.

The field sample results for most individual experiments have not been adjusted for field spike recovery, as originally planned. Adjustment was not needed because the mean field spike recoveries were so close to 100%. Due to the variability of spike recoveries and the presence of outliers in the spike recovery series, it was felt that adjustment for field spike recovery on a per experiment basis would have increased the variability of the field sample results without improving their accuracy.

5.3 Transfers from Carpet by Methods as Described by Their Developers

The first two experiments compared the transfers of freshly dry chlorpyrifos residues from carpet by the cloth roller, the drag sled, and the PUF roller. Each transfer sampling method was performed as described in Table 1, i.e., as conducted by its developers: Ross et al. (1991), Vaccaro and Cranston (1990), and Hsu et al. (1990). This was done to permit intercomparison of transfers among prior studies which employed one of these methods to support registration of pesticides used in the home. It should be noted, however, that these sampling methods differed in characteristics which are likely to affect transfer, such as 20 passes of a roller over a cloth laid on the carpet vs. 2 passes of the PUF roller and 1 pass of the drag sled over a carpet strip.

The transfer method comparisons were conducted on two popular types of new carpet: a nylon plush cut-pile carpet in Experiment 1 and a polypropylene level-loop carpet in Experiment 2. Results of the transfer method comparisons are presented in Table 23 for the nylon plush carpet and in Table 24 for the polypropylene level-loop carpet.

The professional applicator, who performed these applications as well as those for later experiments, was observed to glance over his shoulder frequently to avoid stepping on the deposition coupons, as instructed, as he stepped backward while performing the broadcast application. In addition, it appeared that the applicator sometimes inadvertently applied a double dose of the formulation to the boundary areas between adjacent segments along his application pathway. The variation in deposition coupon amounts and their surface loading estimates sometimes reflected this deposition variability, as for example in Experiment 1. However, in other experiments the deposition coupons may fail to reflect the non-uniformity in the amount applied due to the chance effect of its occurrence relative to the coupon placement. The applicator was never asked to change these practices which contributed to deposition variability on the test flooring.

The variability in formulation deposition produced an inherent variability in the transfer measurements from the test carpets and sheet vinyl. Transfer measurement variability was also affected by the size of the area sampled, due to the averaging effect of sampling a larger area. Thus, measurement using a deposition coupon of a small area was susceptible to greater variation than the mechanical transfer measurements, which encompassed much larger areas of carpet. For example, the coefficient of variation of the deposition coupon measurements was substantially larger than for the mechanical measurements in Experiment 1 (see Table 23). However, transfer measurement variability is reduced by increasing the sampled surface area only to the extent that the deposition variation was randomly distributed over the treated test flooring. Application practices limited the excess deposition to specific overlap locations whose area could exceed the contacted surface area of a transfer measurement. The amount of variation in transfer measurements obtained by a specific method could itself vary substantially from one experiment to another, due solely to whether excess deposition occurred in one or more of the flooring areas pre-designated for collection of the replicate transfer samples. Thus, in this study, inferences based on transfer measurement variability must be drawn with caution. Such inferences may only be warranted when the observed pattern of variation persisted across several experiments.

When performed as described by the method developers, transfers per cm^2 of contacted carpet were highest for the cloth roller, intermediate for the drag sled, and lowest for the PUF roller, both from plush nylon carpet in Experiment 1 and from level-loop polypropylene carpet in Experiment 2. As shown by the coefficient of variation, all three mechanical surface transfer methods gave more repeatable performance on the plush nylon carpet than on the level-loop polypropylene carpet. However, this observation may be an artifact caused by non-uniform application of the chlorpyrifos formulation, as discussed above.

The cloth roller displayed more variation in the transfer of chlorpyrifos residue from the plush nylon carpet than did the drag sled or the PUF roller. However, the coefficients of variation of the rates, in ng/cm^2, of transfer of chlorpyrifos from level-loop polypropylene carpet by the three methods were quite similar in Experiment 2.

Transfers obtained with the cloth roller were larger for rolls oriented with and against the lay of the plush nylon carpet fibers ($\bar{x} \pm s = 780 \pm 140$ ng/cm^2, n=4) than for rolls across the lay of the fibers (430 ± 10 ng/cm^2, n=2) in Experiment 1. In contrast, transfers with the drag sled and the PUF roller were not observed to vary with the orientation of the drag/roll relative to the lay of the carpet fibers in these or later experiments. The additional transfer variation observed with the cloth roller in Experiment 1 can largely be attributed to this directional sampling effect.

5.4 Modification of PUF Roller Sampler

In 1988 SwRI developed a foam roller instrument to simulate pesticide exposure to infants. It was demonstrated that the foam pressed by the roller with a contact rolling motion across an aluminum foil surface has similar characteristics to the human hand in terms of transfer of dried pesticide analytical standard residues (Hsu et al., 1990). EPA evaluated the PUF roller sampler and other methods for monitoring the potential exposure of young children to pesticides in the residential environment in a nine-home pilot study (Lewis et al., 1994). EPA also suggested that a pesticide manufacturer use the instrument to measure dislodgeable residue from turf. The pesticide manufacturer expressed difficulty in using the SwRI instrument, and the EPA evaluation recommended hardware improvements for easier field use. Consequently, SwRI modified the instrument to address the concerns and make it easier to use.

5.4.1 Original Design

The original roller sampler consisted of a ring of polyurethane foam (PUF) surrounding a 3.2 kg stainless steel cylinder. The ring was brought from the laboratory in a glass jar, removed and placed on the cylinder at the sampling site. The cylinder was then bolted to a roller assembly which allowed the user to roll the PUF across the floor. The roller assembly had wheels and was designed to transfer any pressure from the user through the handle to the wheels instead of the PUF ring. Thus, the cylinder remained in contact with the floor at a constant pressure. To acquire samples, the roller assembly was pulled along the floor for a specified distance at a specified speed. When the sampling was complete, the PUF rings were removed and placed in jars for transport to a lab for extraction and analysis.

Comments from users of the instrument indicated some problems. One common concern expressed was that the instrument was difficult to transport to the field due to bulkiness, and it was difficult to assemble at the field site. A ring stand was required for assembly, and bolts had to be removed with a wrench each time a new PUF ring was used. Another user complaint was that there was potential for contamination of the rings when they were removed from the cylinder.

The most important criterion for the new design was that the redesigned instrument should be simple to assemble in the field, preferably with no extra pieces of equipment. A means of rapidly mounting the PUF ring on the roller and removing the PUF ring after sampling while preventing contamination was also important. Other criteria for the redesign included maintaining the concept of the wheels and handle being connected, allowing the wheels to take any excess force exerted on the handle, while the PUF ring maintains a constant force on the surface.

5.4.2 Design Modifications

The first major design change was to replace the large stainless steel cylinder with a smaller aluminum cylinder and a separate weight block. The cylinder is the same width as the foam ring, preventing the foam from being contaminated when it is slid on or off the cylinder. This is particularly important if the instrument is used outdoors where the potential for cylinder contamination would be greater. The weight of the original stainless steel cylinder created the desired pressure through the foam onto the surface. With a smaller aluminum cylinder, a separate weight was necessary to create the required pressure. The weights were fashioned of stainless steel blocks and mounted on arms supporting the aluminum cylinder (see Figure 3). By having separate weight blocks, the pressure exerted on the surface could be varied (see Experiment 5B).

Another feature that was modified was the method of attaching the cylinder to the instrument. The original design used hex nuts which were cumbersome and time consuming to remove and replace. The new design utilizes spring clips and grooves which hold the cylinder in place when it is being rolled across a surface, but allow the user to "snap" the cylinder in and out of the instrument. The support bars to which the cylinder attaches have grooves on the underside to hold the cylinder. The support bars can be angled backwards to allow the cylinder to be replaced easily. This is shown in Figure 5.

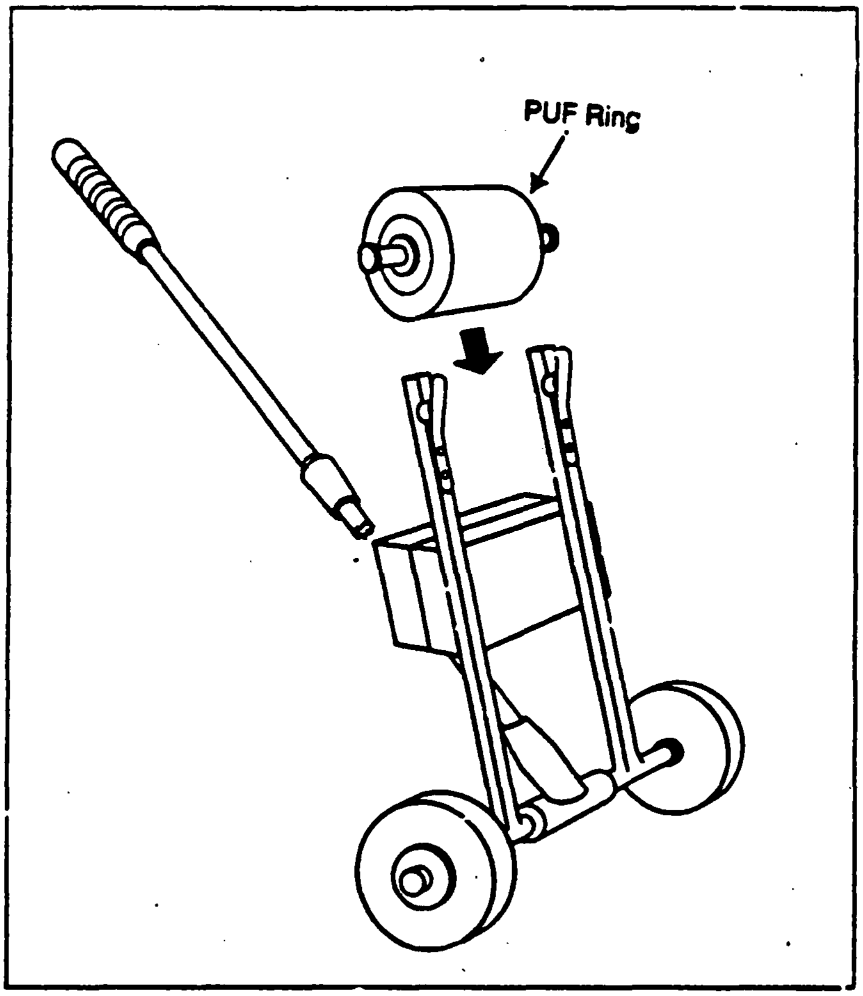

Figure 5. Details of cylinder/frame assembly of modified PUF roller sampler.

The original PUF roller sampler was redesigned to allow for easier use on indoor surfaces as well as for outdoor use. We decided to enlarge the wheels to provide easier rolling across uneven surfaces often experienced outdoors. If a rock or other obstacle gets in front of the wheels, the larger diameter and higher axle allow the instrument to roll over the obstacle with little resistance.

To facilitate transport to a field site, the handle was fabricated to be detachable. The handle was made in two pieces which screw together, and the lower handle piece screws into a fitting on the axle. The handle pieces are 54 and 59 cm long. When disassembled, the length of the base is 32 cm. In addition, since the long stainless steel cylinder was replaced by a shorter aluminum cylinder, the overall width of the instrument could be reduced to 23 cm. (The original model has a base of 72 cm x 37 cm, which includes the non-removable handle.)

5.5 Effect of Moistened Contact Media on Transfers from Carpet: Experiment 3

Moistening the medium in contact with a treated carpet should provide an indication of the transfer which occurs when a child crawls on a carpet with hands which s/he has recently mouthed. The effect on transfers of chlorpyrifos residues from a new plush nylon carpet of pre-moistening the contact surfaces of the denim drag cloth and the PUF roller cover were investigated in Experiment 3.

The results of this experiment are presented in Table 25. After moistening the contact surface with a water aerosol spray, the mean transfer rate increased moderately (ca. 60%) with the drag sled, but markedly (8-fold) with the PUF roller. The greater proportional increase using the moistened PUF roller appears to reflect the 10-fold larger moisture content of the moistened PUF ring (5 g) than the moistened drag cloth (0.5 g), rather than their similar moisture transfers onto a glass surface. As indicated by the coefficient of variation, the measurement variability of both methods increased substantially when moist contact media were used. The increased measurement variation with moistened media may be a serious impediment to the use of moistened media in field studies, since many more replicates would be required to detect a difference in transfer rates. The increased variability was a factor in our decision to perform all subsequent floor transfer experiments using dry contact media.

5.6 Field Performance of the Transfer Sampling Methods Using Dry and Moistened Contact Media

The strengths and weaknesses of each of the three dislodgeable residue methods which were observed while conducting these experiments are summarized in Table 26. Though it is simple in design and configured from readily available materials, the California cloth roller method consistently showed some inherent weaknesses. It was difficult and cumbersome to operate due to the heavy weight of the roller and the fact that operation required the user to be on his/her knees during sample collection. Additionally, during the rolling process, the cloth sample collection medium had a tendency to shift on the carpet out of the targeted sample area, and the plastic sheet between the cloth and the roller would adhere to the roller due to static electricity. The drag sled is also simple in design and constructed from readily available materials. Operation of the drag sled was simplest of the three methods, though the transfer mode from carpet to sample medium relies on friction from rubbing of two surfaces rather than on the rolling contact of the two other methods. For small surfaces or in areas of limited access, the drag sled requires the least amount of room to collect a surface sample. The PUF roller is the most complex device and is expensive to build or purchase. However, it should show the fewest inconsistencies between operators since it is simple to use and has the fewest operational variables.

In the experiments using moistened media with the drag sled and PUF roller methods, uniform moistening of the sample media may not have been achieved. Even though the medium was contacted with a known mass of water, the uniformity of its distribution on the sampling surface of the medium could not be verified.

5.7 Effects of PUF Roller Sampling Variables on Chlorpyrifos Transfer from Carpet

Transfer sampling with the PUF roller had usually been performed by making two passes (over and back) or one pass over a 1.0 m strip of the sampled carpet, at a pressure of 7,300 to 8,300 Pa through the PUF ring and at a speed of about 0.10 m/s over the carpet. Although the number of passes, the length of the carpet strip contacted by PUF roller, the contact pressure, and the roller speed may affect the amount transferred, the effects of these sampling variables on transfer had not previously been studied. Experiments 5A, 5B, and 5C were performed to investigate the effects of these PUF roller sampling variables on transfer of freshly dried chlorpyrifos residue from plush carpet. The designs of the experiments were given in Tables 6, 7, and 8.

5.7.1 Effect on Transfer of Number of Passes by PUF Roller over a Carpet Strip: Experiment 5A

The transfers obtained with increasing number of PUF roller passes over a 1.0 m strip of treated carpet are presented in Table 27. Since the PUF roller is usually placed on the sampled surface in the starting location for several seconds before sampling commences, the mean amount transferred to the PUF roller while stationary on the carpet for 3 s (1.27 µg, from Experiment 5C) was subtracted from each crude transfer amount. The mean adjusted chlorpyrifos amounts transferred were 9.9 µg for one pass, 26 µg for two passes, 49 µg for four passes, 77 µg for eight passes, and 172 µg for twenty passes. Transfer variability among replicates remained large, presumably due to non-uniform deposition. The additional amount transferred to the PUF roller with each additional pass remained approximately 10 µg/pass, from the first pass through the twentieth pass. At the applied chlorpyrifos loading (23 µg/cm^2), each sampled carpet strip contained about 18 mg of chlorpyrifos. This reservoir of chlorpyrifos in the nylon plush carpet was sufficient to yield a relatively constant additional transfer of about 10 µg with each pass of the PUF roller sampler.

5.7.2 Effects on Transfer of Contact Pressure and Speed of PUF Roller: Experiment 5B

The contact pressure of the PUF ring with the treated carpet was varied by removing the weight blocks (2,400 Pa) and by adding additional weights (18,000 Pa). The results of Experiment 5B are summarized in Table 26. The transferred chlorpyrifos amount increased from 8.0 ± 1.4 µg at 2,400 Pa, to 26.8 ± 5.2 µg at 7,300 Pa, and to 46.6 ± 17.8 µg at 18,000 Pa. The increase in PUF roller transfer amount was proportional to the contact pressure.

Replicate runs at a more rapid sampling speed of 30 cm/s were also performed, while using the standard 7,300 Pa pressure. PUF roller transfer was slightly less (21.4 ± 5.8 µg) at 30 cm/s than at 10 cm/s (26.8 ± 5.2 µg).

5.7.3 Effect on Transfer of Length of Carpet Strip Traversed by PUF Roller: Experiment 5C

The carpet strip traversed by the PUF roller to collect a sample was lengthened from 0 cm (stationary for 3 s) to 25 cm, 1.0 m, 3.0 m, and 10.0 m to evaluate its effect on transfer. After subtracting the mean stationary transfer of 1.27 µg, the mean transfer amount increased from 2.1 µg over 25 cm to 11.4 µg over 1.0 m, 57 µg over 3.0 m, and 79 µg over 10.0 m. The amount of transfer to the PUF ring increased quite uniformly with distance traversed over the first 3 m of treated plush nylon carpet, but increased slowly as more carpet was traversed.

5.8 Effects of Drag Sled Sampling Variables on Chlorpyrifos Transfer from Carpet

The effects of varying the contact pressure, traverse speed, and traverse distance of the drag sled on the transfer of fresh dry chlorpyrifos residues from nylon plush carpet to the dragged cloth were investigated in Experiments 5D and 5E.

5.8.1 Effects on Transfer of Contact Pressure and Speed of Drag Sled: Experiment 5D

Increasing the contact pressure exerted by the drag sled on a treated nylon plush carpet had very little effect on the transfer of chlorpyrifos residue to the cloth: from 36 ± 13 µg at 2,100 Pa, to 56 ± 28 µg at 4,500 Pa, and to 43 ± 10 µg at 15,600 Pa (Table 30). Increasing the traverse speed of the drag sled at 4,500 Pa appears to reduce the amount of chlorpyrifos transferred, from 56 ± 28 µg at 7 cm/s to 31 ± 21 µg at 20 cm/s (Table 30).

5.8.2 Effect on Transfer of Length of Carpet Strip Traversed by Drag Sled: Experiment 5E

When placed stationary on the carpet for 3 s (as is often done before sampling commences), a mean of 0.63 µg of chlorpyrifos transferred to the cloth beneath the drag sled (Table 31). This is about half the mean of 1.27 µg transferred to the PUF ring beneath the stationary PUF roller in 3 s. The mean transfer amount to the drag cloth increased from 4.2 µg over the first 17 cm traversed, to 0.86 µg over 92 cm, 124 µg over 2.9 m, and 302 µg over 9.8 m. Although it was low on the 92 cm traverse, the amount of transfer from the treated plush carpet increased relatively uniformly with distances up to 10 m traversed by the drag sled.

5.9 Effect of Temperature on Transfer of Pesticide Residues from Carpet

Experiments 5A through 5E were intentionally performed over a 9 °C range of indoor air temperatures to permit an estimate of the effect of air temperature on transfer of fresh chlorpyrifos residue from plush carpet by the PUF roller and the drag sled. However, application variability and possible effects of uncontrolled variables between the experiments confounded the apparent effect of air temperature. Consequently, additional experiments were designed and conducted to investigate the specific effect of temperature on transfers by the PUF roller and by the drag sled of both aged residues (applied 31 to 37 days earlier, Experiment 8A) and fresh residues (Experiment 8B) of chlorpyrifos, piperonyl butoxide, and pyrethrin I from nylon plush carpet.

5.9.1 Effect of Temperature on Transfer of Aged Residues: Experiment 8A

The plush carpet had been treated with chlorpyrifos, piperonyl butoxide, and pyrethins 37 days prior to Experiment 8A (for Experiment 6A) and again with piperonyl butoxide and pyrethrins 31 days before Experiment 8A (for Experiment 6B). Experiment 8A involved triplicate transfer sampling of the carpet with both the drag sled and the PUF roller, first at cool carpet and indoor air temperatures, followed by repeat sampling at moderate and hot temperatures (see Table 13). The mean indoor air temperature increased from 17 °C to 27 °C to 34 °C, while the mean carpet temperature increased less rapidly from 22 °C to 27 °C to 31 °C during the three sampling blocks. Transfer results are discussed in relation to the carpet temperature, which we consider the more relevant temperature measurement. The results are presented in Tables 32 (chlorpyrifos), 33 (piperonyl butoxide), and 34 (pyrethrin I). Substantial transfer measurement variability obscures clear trends. Mean transfers of aged chlorpyrifos residues increased by approximately a factor of 2 as the carpet temperature was raised from 22 °C to 31 °C: from 0.46 μg to 1.05 μg with the drag sled and from 0.43 μg to 0.78 μg with the PUF roller. Transfers with the drag sled also increased by about a factor of 2 for aged piperonyl butoxide and a factor of 1.5 for aged pyrethrin I with this rise in carpet temperature. However, transfers with the PUF roller of aged piperonyl butoxide and pyrethrin I were basically unchanged with this rise in carpet temperature. Air samples taken during the cool and hot sampling periods showed that the indoor air concentrations of chlorpyrifos and piperonyl butoxide more than doubled with this temperature rise.

5.9.2 Effect of Temperature on Transfer of Fresh Residues: Experiment 8B

After a formulated mixture of chlorpyrifos, piperonyl butoxide, and pyrethrins had dried on the plush carpet, triplicate transfer samples were again collected with the drag sled and the PUF roller at cool, moderate, and hot indoor temperatures (see Table 14). The mean carpet temperatures were 23 °C, 27 °C, and 30 °C during the three sampling periods. Coupon-adjusted transfers of chlorpyrifos increased from the cool to the hot carpet temperature by 21% (from 11.2 μg at 23 °C to 13.6 μg at 30 °C) with the drag sled and by 35% (from 5.1 μg to 6.9 μg) with the PUF roller (Table 35). The corresponding increases in coupon-adjusted transfers of piperonyl butoxide were 47% (from 15.0 μg to 22.1 μg) with the drag sled and 37% with the PUF roller (Table 36). The increase in pyrethrin I transfers was slightly larger: 61% with the drag sled and 54% with the PUF roller (Table 37). The larger transfers obtained in the fresh residue experiment may be responsible for the more consistent transfer increase with rising carpet temperature observed for fresh residues than for aged residues.

5.10 Reduction in Transfer of Pesticide Residues from Carpet with Time after Application

Transfer samples of residues remaining on the plush carpet were usually collected in duplicate with the drag sled and the PUF roller just prior to cleaning the carpet for the next experiment. One objective was to obtain an estimate of the reduction in transfer of the residue with time after application. This was achieved by comparing the mean transfer amounts on the day of application and on the subsequent day before cleaning. All of the data relevant to reduction in chlorpyrifos transfer with time after application is presented in Table 38. In the seldom-used trailer, chlorpyrifos transfers from the plush carpet with the drag sled were reduced by an order of magnitude within a month after application and by two orders of magnitude after three months. Chlorpyrifos transfers from the same carpet with the PUF roller declined more gradually with time after application, but still approached two orders of magnitude after three months. The simultaneous reduction in transfers of piperonyl butoxide (Table 39) and pyrethrin I (Table 40) from the same plush carpet was similar to the reduction in chlorpyrifos transfer within the first month after application.

5.11 Effect of Carpet Cleaning on Transfer of Chlorpyrifos Residues

The plush nylon carpet used in Experiment 3 was commercially cleaned by water extraction before each of eight subsequent chlorpyrifos applications. The pair of duplicate chlorpyrifos transfer samples collected by the same method just before cleaning and again just before the application (usually 48 to 72 hrs after cleaning to allow the carpet to dry) can be used to assess the effectiveness of the carpet cleaning in reducing chlorpyrifos residues on the carpet surface. The mean chlorpyrifos transfers before and after cleaning are shown in Table 41. The first three cleanings produced substantial reductions (4- to 15-fold) in chlorpyrifos transfer from the carpet. However, the fifth, seventh, and eighth cleanings did not reduce surface chlorpyrifos transfer from the carpet at all. It is unclear whether residue build-up in the trailer or incomplete drying after cleaning contributed to the apparent ineffectiveness of the later cleanings.

5.12 Efficiency of Removal of Chlorpyrifos and Pyrethrin I Residues from Human Skin by the Isopropanol Handwipe Method

5.12.1 Determination of Wipe Removal Efficiency

The merits and limitations of a mass balance approach to determination of removal efficiency for hand washes and wipes have recently been discussed by Fenske et al. (1994). Initial experiments were performed to determine the efficiency of the procedure for the removal of pesticides from human hands. Natural pyrethrins and chlorpyrifos were selected for this portion of the study since they are common pesticides used in the home. Natural pyrethrins is a mixture of six compounds. The most abundant, pyrethrin I, was selected to be quantitated for this experiment. The removal efficiency (RE) for a particular pesticide is calculated by:

$$RE = (M_{wipe} / E_{ext}) / [M_{app} - (M_{foil} / E_{el})]$$

where M_{wipe} is the mass of pesticide found on the wipe, M_{app} is mass of the pesticide applied to the foil, M_{foil} is mass of pesticide remaining on the foil, E_{ext} is the mean extraction efficiency of the pesticide from the wipe material and E_{el} is the efficiency of eluting the pesticide from the aluminum foil square.

E_{el} for chlorpyrifos and pyrethrins from the aluminum foil squares was determined by spiking seven foil squares, each with two levels of the pesticides using the procedure described above. The foils were then extracted and the amounts of the two compounds recovered were calculated. The recovery for each foil was calculated by dividing the recovered amount by the spiked amount, which was determined by three replicates of direct analysis of the spiking solution dissolved in 10% ether in hexane. The means and standard deviations for E_{el} for each analyte at each level were then calculated. These results are given in the upper half of Table 42. Mean E_{el} for chlorpyrifos were 105 ± 18% and 100 ± 7% for 1.86 µg and 23.9 µg spiked respectively. Pyrethrin I recoveries were 103 ± 26% and 100 ± 11% for 17.5 µg and 246 µg spiked. For both chlorpyrifos and pyrethrin I, the recovery decreases from replicate 1 to replicate 7. This is most likely attributed to calibration drift of the GC/MS. To partially compensate for this drift, standards were analyzed at the beginning and end of the sequence and the response factor was taken as the average of the response factors for the two standards. Within the experimental error, both analytes were quantitatively recovered from the aluminum foil.

E_{ext} was determined for chlorpyrifos and pyrethrin I by spiking seven replicates each with two different amounts of the formulated mixture. The wipes were then extracted and the amount of chlorpyrifos and pyrethrin I extracted was determined by GC/MS. The lower half of Table 42 shows E_{ext} for each wipe replicate, and the mean and standard deviation for each analyte spike level. Pyrethrin I was extracted with mean recoveries of 97 ± 14% and 101 ± 9% for spiking levels of 16.1 and 319 µg. Chlorpyrifos was extracted with recoveries of 88 ± 6% and 100 ± 4% for spike levels of 1.93 and 25.2 µg. Within experimental error, pyrethrin I was quantitatively extracted from the wipe material at both high and low levels. Chlorpyrifos recovery was quantitative at the higher spike level. However, it is apparent that the extraction procedure was not as successful in removing the chlorpyrifos when applied at a level near 2 µg.

At each stage of the wipe process, blanks were analyzed. No target pesticides were found at a level above the detection limit in extraction solvent, blank foil squares or blank dressing sponges when these materials were extracted and analyzed by GC/MS. In addition to these matrix blanks, handwipe control blanks were performed on two days during the hand-press experiments. In this experiment, the subjects hands were pressed onto clean aluminum foil squares then wiped using the handwipe procedure. These results are shown in Table 17. No pyrethrin I was found in the control blanks above the detection limit. However, chlorpyrifos at levels ranging from 0.10 to 0.38 µg were found in each of the eight control blanks. At this time, the source of the chlorpyrifos in the controls is unclear. Chlorpyrifos is used extensively in the southern United States for indoor and outdoor insect control. One possibility is that the chlorpyrifos was introduced onto the subjects hands by touching a contaminated object, such as the faucet or the soap bar during hand washing prior to the experiment. A more likely explanation is that these blank values represent ambient levels of chlorpyrifos. The chlorpyrifos may not be removed with soap and water since it is deeply imbedded in the fats and oils in the skin. However, these fats and oils containing the chlorpyrifos are removed from the hands using the 2-propanol wipe.

Once E_{el}, E_{ext}, and blank levels for each portion of the experiment were understood, the RE for chlorpyrifos and pyrethrin I were experimentally determined using the procedure described above. Results for the RE of chlorpyrifos are given in Table 43. The amount of chlorpyrifos spiked on the foil was determined from the mean of six analytical results, obtained from three analyses each of two solutions prepared by dilution of the spiking solution in 1:1 diethyl ether:hexane. The amount of chlorpyrifos left on the foil was determined by extraction of the foil square and has been corrected for E_e, and blank results. The amount of chlorpyrifos placed on the hand was calculated as the difference between the amount spiked on the foil and the amount remaining on the foil. The amount removed by handwipe was the analytical result obtained from the handwipe corrected for blank and E_{ext} results. The percent removed was the amount of chlorpyrifos placed on the hand divided by the amount removed by the handwipe. The RE ranged from 85 to 119% over the course of the three days of the experiment. The mean RE for chlorpyrifos was found to be 104 ± 11% for the twelve measurements. RE results for pyrethrin I are given in Table 44. A wider variation in the removal efficiency was observed with results ranging from 56 to 144%. The mean RE for the twelve measurements was 92 ± 28%.

5.12.2 Discussion

Hand washes have been employed to monitor hand exposure to pesticides, but they require the handling of large volumes of solvent and are also difficult to use on young children (Lewis et al. 1994). Hand wash studies using chlorpyrifos showed recoveries of 30% with ethanol and 43% with 10% 2-propanol in water after immediate exposure to dried formulation (Fenske et al. 1994). Our results for wipe removal efficiency using 2-propanol are significantly higher. We attribute the high removal efficiency of our technique to a combination of the solvation of the pesticides by the undiluted 2-propanol and the mechanical removal by the wiping action. Once the wipe has been performed, the dressing sponges are kept moist with 2-propanol. This prevents strong bonding of the polar pesticides to the cellulose material and enhances extraction efficiency.

At this time, removal efficiencies following an extended period of time after exposure (i.e., 30 min) have not been performed. However, based upon control blank results presented in Table 17, it is anticipated that the described controlled double wipe procedure may efficiently extract pesticides deeply embedded in the skin.

The efficiency of dermal penetration of a particular pesticide depends upon the type and concentration of the pesticide, the solvent and surfactant used and the physical form of the formulation. Concerns have been raised that a 2-propanol wipe may enhance the penetration of certain pesticides through the skin. Experiments should be performed to investigate possible penetration effects and to compare the removal efficiency of a wipe using 100% 2-propanol with wipes using other solvents such as mild aqueous surfactants or diluted alcohol solutions. We would anticipate, however, that these alternative solvents would not be as efficient in removing pesticides that have been incorporated into the fats and oils in the skin.

5.13 Comparison of Transfers of Pesticide Residues from Flooring by the Drag Sled, PUF Roller, and Human Hand Presses

A major objective of this project was to compare mechanical dislodgeable residue methods to presses by the human hand with respect to transfer of formulated pesticide residues from treated flooring. The data to make these transfer comparisons of the drag sled and PUF roller with human hand presses was developed by performing Experiments 6 and 7.

5.13.1 Comparison of Transfers from Plush Carpet: Experiment 6A

Transfers from treated plush carpet by the drag sled, the PUF roller, and a single press of a human hand in Experiment 6A are given for chlorpyrifos residues in Table 45, for piperonyl butoxide residues in Table 46, and for pyrethrin I residues in Table 47. It was difficult to detect the amount transferred to the subjects' hand by a single press through the template onto 48 cm^2 of the treated carpet. The hand transfer of chlorpyrifos was usually less than the mean hand wipe background of 0.26 μg on Experiment 6A field blanks. Similarly, the hand transfer of piperonyl butoxide seldom exceeded the detection limits of the hand press sample and the hand wipe field blank. Pyrethrin I was not detected in any single hand press samples. It would have been desirable to determine hand transfer based on a single press, as attempted in this experiment, in order to avoid the possibly non-additive accumulation of residue transfer with additional presses onto adjacent carpet sections. However, lack of transfer detection with a single hand press rendered this approach infeasible. Instead, Experiment 6B was planned and conducted to obtain the needed transfer comparison of the drag sled and PUF roller to the hand press. However, Experiment 6A did demonstrate that a single pass of the drag sled gave a 3- to 4-fold greater transfer of all three formulated pesticides from the treated plush carpet than did a single pass of the PUF roller.

5.13.2 Comparison of Transfers from Plush Carpet: Experiment 6B

For Experiment 6B, a formulation of methoprene, piperonyl butoxide, and natural pyrethrins was applied by aerosol spray can to the same plush carpet used in Experiment 6A on the fourth day after its completion, without recleaning the carpet. The same sampling design was used, except that each hand palm was pressed onto ten adjoining areas of the treated carpet through an elongated template. The transfer comparisons from Experiment 6B are given for chlorpyrifos, methoprene, piperonyl butoxide, and pyrethrin I in Tables 48 through 51, respectively. The transfer rate of each pesticide from the plush carpet was largest for the drag sled, intermediate for the PUF roller, and smallest for the human hand press. For example, the average transfer rates in ng/cm^2 were 9.2 (drag sled), 2.9 (PUF roller), and 1.3 (hand press) for chlorpyrifos, and 128 (drag sled), 58 (PUF roller), and 17 (hand press) for piperonyl butoxide. Transfer rates appeared more variable for the hand press than for the drag sled or PUF roller.

5.13.3 Comparison of Transfers from Sheet Vinyl: Experiment 7

The same experimental design was also used to compare pesticide residue transfers from sheet vinyl. The transfer comparisons from Experiment 7 are given for chlorpyrifos, piperonyl butoxide, and pyrethrin I in Tables 52 through 54, respectively. Similar to the transfers from carpet, the transfer rate of each pesticide from the sheet vinyl was largest for the drag sled, intermediate for the PUF roller, and smallest for the human hand press. For example, the average transfer rates in ng/cm^2 were 1890 (drag sled), 780 (PUF roller), and 255 (hand press) for chlorpyrifos, and 192 (drag sled), 116 (PUF roller), and 39 (hand press) for pyrethrin I.

5.13.4 Summary of Transfer Comparisons

The means and standard deviations of the transfer rates obtained in Experiments 6A, 6B, and 7 are presented in Table 55. This table illustrates that the transfer rate was consistently largest for the drag sled, intermediate for the PUF roller, and smallest for the human hand press, for all types of flooring and pesticides examined.

5.14 Comparison of Percent Mean Transfers of Pesticide Residues from Flooring by Mechanical and Hand Press Methods

5.14.1 Percent Mean Transfers of Chlorpyrifos

Chlorpyrifos transfers from flooring were measured in most of the sampling experiments. The mean transfer of the applied chlorpyrifos residue, defined as the ratio of the mean transfer rate (ng/cm^2) to the mean surface loading (ng/cm^2) is given by experiment and transfer method in Table 56. The percent mean transfer of chlorpyrifos is much greater from sheet vinyl than from carpet. Inspection suggests that the percent of chlorpyrifos transferred from new carpet (Experiments 1-3) may be larger than the percent transferred from used carpet (Experiments 5A-5E, 6A, and 8B), since this pattern was observed both with the drag sled and the PUF roller.

5.14.2 Comparison of Percent Mean Pesticide Residue Transfers in Experiments 6 and 7

The percent mean transfers of the pesticides applied to carpet and sheet vinyl in Experiments 6 and 7 are presented in Table 57. A given method (drag sled, PUF roller, or hand press) transferred virtually the same percentage of applied residue of all the formulation's active ingredients from the treated flooring in a given experiment. The percent transferred from sheet vinyl after broadcast application (Experiment 7) was nearly an order of magnitude larger than the percent transferred from plush carpet after aerosol can application (Experiment 6B), and two or more orders of magnitude larger than the percent transferred from plush carpet after broadcast application (Experiment 6A). There was more than an order of magnitude greater transfer of dried residues from plush carpet after application of an aerosol can formulation (Experiment 6B) than after broadcast application of a water-based formulation (Experiment 6A). These major effects of flooring and application method (or formulation) on percentage transfer were found by all three methods.

5.14.3 Stability of the Ratio of Mechanical and Hand Press Transfers

Table 57 indicates that the transfer efficiency is about three times higher for the drag sled than for the PUF roller, and about three times higher for the PUF roller than for the hand press, for every active ingredient, flooring, and application method investigated. To obtain a more precise estimate of this relationship, the ratio of the mechanical method transfer mean (n=2) to the simultaneous hand press transfer mean (n=6) was calculated for the 17 specific sets of pesticide within day within experiment for which hand transfers were measurable. The transfer rates and ratios are presented in Table 58. Both the drag sled/hand press ratio and the PUF roller/hand press ratio are quite stable over the broad range of transfer rates obtained in these 17 sets. The mean ± standard deviation of these ratios were 7.4 ± 2.8 for drag sled/hand press and 3.3 ± 2.1 for PUF roller/hand press.

These observations indicate that the PUF roller and the drag sled can both be used to estimate transfers of formulated pesticide residues from flooring to a human hand by press contact. Crude estimates of the transfer to human skin of residues of pesticides recently applied to a floor surface can be calculated from drag sled or PUF roller measurements of the surface, by dividing by the appropriate mean transfer ratio given in Table 58.

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Table 1. Characteristics of Dislodgeable Residue Methods as Described by Developer and Used for Experiments 1 and 2

Property	California Cloth Roller	Dow Drag Sled	SwRI PUF Roller
Sampling medium (material)	Percale bedsheet (50% cotton, 50% polyester)	Denim weave cloth (predominantly cotton)	Polyurethane foam ring (polyether, 0.029 g/cm^3)
Surface of sampling medium	Square $(42.9\ cm)^2$	Square $(10.2\ cm)^2$	Curved exterior of ring, (OD = 8.9 cm, length = 7.6 cm)
Contact motion	Roll	Drag	Roll
Face (instantaneous contact area pressed through sampling medium)	$440\ cm^2 = 42.9\ cm \times 10.2\ cm$	$58\ cm^2 = (7.6\ cm)^2$	$38.6\ cm^2 = 7.6\ cm \times 5.1\ cm$
Mass exerting pressure through sampling medium	14.4 kg	3.46 kg	3.25 kg;[a] 3.10 kg[b]
Pressure exerted through sampling medium	$2{,}300\ Pa = (14.4\ kg)(9.8\ m/s^2)/[(0.61\ m)(0.10\ m)]$	$5{,}900\ Pa = (3.46\ kg)(9.8\ m/s^2)/(0.076\ m)^2$	8,300 Pa;[a] 8,000 Pa[b] $= (3.10\ kg)(9.8\ m/s^2)/[(0.076\ m)(0.05\ m)]$
Sampled carpet area	$0.184\ m^2 = (0.429\ m)^2$	$0.093\ m^2 = 0.076\ m \times 1.22\ m$	$0.076\ m^2 = 0.076\ m \times 1.0\ m$
Number of passes over sampled carpet area	20	1	2
Sampling speed over carpet	0.23 m/s	0.07 m/s	0.10 m/s

a Original PUF roller sampler
b 1992 model of PUF roller sampler

Table 2. Characteristics of Dislodgeable Residue and Hand Press Methods as Used for Experiment 7

	Drag Sled	PUF Roller (October 1992 Model)	Human Hand Press
Sampling medium	Denim weave cloth (predominantly cotton)	Polyurethane foam (PUF) ring ($0.029\ g/cm^3$, polyether)	Skin on palm of hand
Surface of sampling medium	Square $(10.2\ cm)^2$	Curved exterior of ring(OD = 8.9 cm, length = 7.6 cm)	Palm (ca. 8 cm × 8 cm)
Contact motion	Drag	Roll	Ten presses (for 1 s)
Face (instantaneous pressed contact area through sampling medium)	7.6 cm × 7.6 cm = $58\ cm^2$	7.6 cm × 5.1 cm = $38.6\ cm^2$	7.6 cm × 7.6 cm = $58\ cm^2$
Mass exerting pressure through sampling medium	3.46 kg	3.10 kg	NA
Pressure exerted through sampling medium	5,900 Pa = $(3.46\ kg)(9.8\ m/s^2)/(0.076\ m)^2$	8,000 Pa = $(3.10\ kg)\ (9.8\ m/s^2)/\ (0.076\ m)\ (0.05\ m)]$	6,900 Pa = 1.0 psi
Sampled carpet area	7.6 cm × 1.0 m = $0.076\ m^2$	7.6 cm × 1.0 m = $0.076\ m^2$	10 × 7.6 cm × 6.3 cm = $0.048\ m^2$
Number of passes over sampled carpet area	1	1	1
Sampling speed over carpet	0.07 m/s	0.10 m/s	NA

Table 3. Pesticide Applications to Flooring for Experiments

Experiment	Treatment Date	Flooring Material	Applied Formulation	Active Ingredients	Deposition Rate[a] ($\bar{x} \pm s$) μg/cm²
1	8-4-92	Plush carpet (new)	Dursban L.O.	Chlorpyrifos (0.5%)[b]	13.5 ± 8.2
2	8-10-92	Level-loop carpet (new)	Dursban L.O.	Chlorpyrifos (0.5%)	10.6 ± 1.2
3	11-24-92	Plush carpet (new)	Dursban L.O.	Chlorpyrifos (0.5%)	19.8 ± 3.3
5A	3-2-93	Plush carpet (used)	Dursban L.O.	Chlorpyrifos (0.5%)	23.4 ± 1.1
5B	3-9-93	Plush carpet (used)	Dursban L.O.	Chlorpyrifos (0.5%)	26.6 ± 1.3
5C1	3-16-93	Plush carpet (used)	Dursban L.O.	Chlorpyrifos (0.5%)	12.8 ± 0.8
5C2	3-25-93	Plush carpet (used)	Dursban L.O.	Chlorpyrifos (0.5%)	23.5 ± 4.2
5E1	4-20-93	Plush carpet (used)	Dursban L.O.	Chlorpyrifos (0.5%)	24.0 ± 11.1
5E2	4-27-93	Plush carpet (used)	Dursban L.O.	Chlorpyrifos (0.5%)	31.3 ± 0.04
5D	5-19-93	Plush carpet (used)	Dursban L.O.	Chlorpyrifos (0.5%)	31.2 ± 5.6
6A	6-16-93	Plush carpet (used)	Dursban L.O.	Chlorpyrifos (0.25%)	5.4 ± 0.9
			Kicker	Piperonyl butoxide (0.25%)	5.3 ± 1.0
				Pyrethrin I (0.025%)	0.85 ± 0.15
6B	6-22-93	Plush carpet (used)	Siphotrol[c]	Methoprene (0.015%)	0.11 ± 0.01
				Piperonyl butoxide (1.0%)	5.4 ± 0.6
				Pyrethrin I (0.2%)	1.8 ± 0.3
8B	7-29-93	Plush carpet (used)	Dursban L.O.	Chlorpyrifos (0.25%)	5.6 ± 1.6
			Kicker	Piperonyl butoxide (0.25%)	4.5 ± 1.4
				Pyrethrin I (0.025%)	0.68 ± 0.20
7	8-10-93	Sheet vinyl (new)	Dursban L.O.	Chlorpyrifos (0.25%)	8.3 ± 0.5
			Kicker	Piperonyl butoxide (0.25%)	7.3 ± 1.2
				Pyrethrin I (0.025%)	1.4 ± 0.01

a From deposition coupons collected on day of application
b Composition in aqueous spray
c Aerosol spray can

Table 4. Sampling Design of Experiments 1 and 2

Sample Category	Number of Replicates, by Method α-Cellulose Deposition Coupon	Cloth Roller	Drag Sled	PUF Roller	Total Samples
Field blank (pre-application)	1	1	1	1	4
Dursban LO application					
Field samples (begin 2 hours post application)	6	6	6	6	24
Field spikes (at start and end of field sampling)	2	2	2	2	8
Total Samples	9	9	9	9	36

Table 5. Sampling Design of Experiment 3

Sample Category	Number of Replicates, by Method					Total Samples
		Drag Sled		PUF Roller		
	α-Cellulose Deposition Coupon	Dry Cloth	Moist Cloth	Dry PUF	Moist PUF	
Field blank (pre-application)	1[a]	1	1	1	1	5
Dursban LO application						
Replicate field samples (begin 2 hours post application)	5[a]	4	5	4	5	23
Field spikes (at start and end of field sampling)	2[a]	2	2	2	2	10
Total Samples	8[a]	7	8	7	8	38

a Two α-cellulose pads laid out in the block are combined as one sample

Table 6. Sampling Design of Experiment 5A: Effect of Number of Passes of PUF Roller Sampler[a] on Chlorpyrifos Dislodgeable Residue Transfer

Sampling Variables			Number of Samples by Type		
Indoor Air Temp.		Roller Passes	PUF Roller Replicates	Deposition Coupons	Total
Cool (~20°C)		1	3	3[c] (for 1, 2, 4, 8 passes)	
		2	3		
		4	3		
		8	3		
		20	3		
Field Spikes			2	1[c]	
Field Blanks	before carpet cleaned		4[d]	0	
	before chlorpyrifos application		4[d]	0	
			25	4	29

a Normal pressure (7,300 Pa) and speed (0.1 m\s) over 1 m length of carpet
b The room will be segmented into north, central, and south blocks
c Four α-cellulose coupons laid out in quadrants of block are combined as one sample for extraction and analysis
d Two background level samples taken using PUF roller and two background levels taken with the drag sled

Table 7. Sampling Design of Experiment 5B: Effect of Sampling Pressure and Speed of PUF Roller Sampler[a] on Chlorpyrifos Dislodgeable Residue Transfer

Sampling Variables			Number of Samples by Type		
Indoor Air Temp.	PUF Roller Pressure	PUF Roller Speed	PUF Roller Replicates[b]	Deposition Coupons	Total
Warm (~30°C)	2,400 Pa (No weights) (0.35 psi)	0.1 m/s	3	3[c]	
	Normal (Child weight) 7,300 Pa (1.05 psi)	0.1 m/s	3		
	18,000 Pa (Adult weight) (2.6 psi)	0.1 m/s	3		
	Normal 7,300 Pa	Fast (~0.3 m/s)	3		
Field Spikes			2	1[c]	
Field Blanks	before carpet cleaned		2	0	
	before application		2	0	
			18	4	22

a Single pass over 1 m length of carpet
b Segment room into north, central, and south blocks
c Four α-cellulose coupons laid out in quadrants of block are combined as one sample

Table 8. Sampling Design of Experiment 5C: Effect of Carpet Length Traversed by PUF Roller Sampler[a] on Chlorpyrifos Dislodgeable Residue Transfer

Sampling Variables		Number of Samples by Type				
		Day 1		Day 2		
Indoor Air Temp.	Traverse Length	Roller Repl.[b]	Depos. Coupons	Roller Repl.[b]	Depos. Coupons	Total
Moderate (~25°C)	0.0 m (stationary-3 s)	2		2		
	0.25 m (1 revolution of compressed PUF ring)	2		2		
	1.0 m	2	2[c]	2	2[c]	
	3 m	2		2		
	10 m	1		1		
Field Spikes		2	1[c]	2	0	
Field Blanks	before carpet cleaned	2	0	2	0	
	before application	2	0	2	0	
		15	3	15	2	35

a Single pass at normal pressure (7,300 Pa) and speed (0.1 m/s)
b Segment room into north and south blocks
c Four α-cellulose coupons per block

Table 9. Sampling Design of Experiment 5D: Effect of Sampling Pressure and Speed of Drag Sled[a] on Chlorpyrifos Dislodgeble Residue Transfer

Sampling Variables			Number of Samples by Type		
Indoor Air Temp.	Drag Sled Pressure	Drag Sled Speed	Drag Sled Replicates[b]	Deposition Coupons	Total
Warm (25-30°C)	Light weight 2,100 Pa	0.07 m/s	3	3[c] (all four conditions)	
	Normal 4,500 Pa (Child weight) (0.87 psi)	0.07 m/s	3		
	Adult weight 15,600 Pa (2.2 psi)	0.07 m/s	3		
	Normal 4,500 Pa	Fast (0.2 m/s)	3		
Field Spikes			2	1[c]	
Field Blanks	before carpet cleaned		4[d]	0	
	before application		4[d]	0	
			22	4	26

a Single pass over 1 m length of carpet
b Segment room into north, central, and south blocks
c Four α-cellulose coupons laid out in quadrants of block are combined as one sample
d Two background level samples taken using PUF roller and two background levels taken with the drag sled

Table 10. Sampling Design of Experiment 5E: Effect of Carpet Length Traversed by Drag Sled[a] on Chlorpyrifos Dislodgeable Residue Transfer

Sampling Variables			Number of Samples by Type			
		Day 1		Day 2		
Indoor Air Temp.	Traverse Length	Drag Sled Repl.[b]	Depos. Coupons	Drag Sled Repl.[b]	Depos. Coupons	Total
Cool (20-25°C)	0.0 m (stationary-3 s)	2	2[c]	2	2[c]	
	0.25 m	2		2		
	1.0 m	2		2		
	3 m	2		2		
	10 m	1		1		
Field Spikes		2	1[c]	2	0	
Field Blanks	before carpet cleaned	2	0	2	0	
	before application	2	0	2	0	
		15	3	15	2	35

a Single pass at normal pressure (4,500 Pa) and speed (0.07 m/s)
b Segment room into north and south blocks
c Four α-cellulose coupons per block

Table 11. Sampling Design of Experiment 6: Comparison of Chlorpyrifos and Pyrethrins Residue Transfers from Carpet by Drag Sled Sampler, PUF Roller Sampler, and Hand Press by Three Human Subjects

		Number of Samples by Type									
					Hand Press						
					Subject A		Subject B		Subject C		
Day	Sample Category	Deposition Coupon	Drag Sled	PUF Roller	L	R	L	R	L	R	Total
0A	Field blanks	0	2	2	1	1	1	1	1	1	10
0B	Field blanks	0	0	0	1	1	1	1	1	1	6
1-AM	Pesticide application										
1-AM	Field matrix spikes	1[a]	1	1	1		1				5
1-PM	DR samples[b]	2[a]	2	2	1	1	1	1	1	1	12
2-PM	DR samples[b]	2[a]	2	2	1	1	1	1	1	1	12
3-PM	DR samples[b]	2[a]	2	2	1	1	1	1	1	1	12
3-PM	Field matrix spike	1[a]	1	1	1		1				5
Total DR Samples		6	6	6	6		6		6		36
Total Field Blanks		0	2	2	4		4		4		16
Total Field Matrix Spikes		2	2	2	2		2		0		10
Total Samples		8	10	10	12		12		10		62

a The two α-cellulose coupons in a block are combined and extracted together as a single sample
b The samples collected from different treated carpet areas within each block are two deposition coupons, one drag sled, one PUF roller and one press/wipe by each subject of the same hand

Table 12. Sampling Design of Experiment 7: Comparison of Chlorpyrifos and Piperonyl Butoxide Residue Transfers from Sheet Vinyl Flooring by Drag Sled Sampler, PUF Roller Sampler, and Hand Press by Three Human Subjects

		Number of Samples by Type									
					Hand Press						
					Subject A		Subject B		Subject C		
Day	Sample Category	Deposition Coupon	Drag Sled	PUF Roller	L	R	L	R	L	R	Total
1	Field blanks	0	0	0	1	1	1	1	1	1	6
2	Field blanks	0	2	2	1	1	1	1	1	1	10
3-AM	Pesticide application										
3-AM	Field matrix spikes	1[a]	1	1	1		1				5
3-PM	DR samples[b]	2[a]	2	2	1	1	1	1	1	1	12
4-PM	DR samples[b]	2[a]	2	2	1	1	1	1	1	1	12
5-PM	DR samples[b]	2[a]	2	2	1	1	1	1	1	1	12
5-PM	Field matrix spike	1[a]	1	1	1		1				5
Total DR Samples		6	6	6	6		6		6		36
Total Field Blanks		0	2	2	4		4		4		16
Total Field Matrix Spikes		2	2	2	2		2		0		10
Total Samples		8	10	10	12		12		10		62

a The two Teflon coupons in a block are combined and extracted together as a single sample

b The samples collected from different treated vinyl areas within each block are two deposition coupons, one drag sled, one PUF roller and one press/wipe by each subject of the same hand

Table 13. Sampling Design of Experiment 8A: Effect of Temperature on Transfer of Aged Residues

Category	Condition (Time)	Number of Samples by Type: Drag Sled	PUF Roller	Air Sample	Total
Field Matrix Spike	Start (AM)	1	1		2
Dislodgeable Residue Samples[a]	Cool (~20°C) (Late AM)	3	3	1 (16h)	7
DR Samples[a]	Moderate (25-27°C) (Early PM)	3	3		6
DR Samples[a]	Hot (30-35°C) (Late PM)	3	3	1 (4h)	7
Field Matrix Spike	Finish	1	1	—	2
Total Field Samples		9	9	2	20
Total Field Matrix Spikes		2	2	0	4
Total Samples		11	11	2	24

a Measure temperature of air (6 in. above carpet) and carpet at beginning and end of each sample set

Table 14. Sampling Design of Experiment 8B: Effect of Temperature on Transfer of Fresh Residues[a]

Sample Category	Condition (Time)	Number of Samples by Type: Deposition Coupon	Drag Sled	PUF Roller	Air Sample	Total
Field Blanks	Pre-application (~8 AM)	0	3	3	0	6
Pesticide Application[a]	(~8:30 AM)					
Field Matrix Spike	Start (~10:30 AM)	1[b]	1	1	0	3
Dislodgeable Residue Samples[c]	Cool (~20°C) (Late AM)	2[b]	3	3	1 (2h)[c]	9
DR Samples[c]	Moderate (25-27°C) (Early PM)	2[b]	3	3	0	8
DR Samples[c]	Hot (30-35°C) (Late PM)	2[b]	3	3	1 (2h)[c]	9
Field Matrix Spike	Finish	1[b]	1	1	0	3
Total Field Samples		6	9	9	2	26
Total Field Blanks		0	3	3	0	6
Total Field Matrix Spikes		2	2	2	0	6
Total Samples		8	14	14	2	38

a Chlorpyrifos (0.25%), pyrethrins (0.025%), and piperonyl butoxide (0.25%) broadcast at 1 gal/1600 ft^2
b The two α-cellulose coupons in a block are combined and extracted together as a single sample
c Measure temperature of air (6 in. above carpet) and carpet at beginning and end of each sample set

Table 15. Sampling Design of Experiment 4: Determination of Handwipe Removal Efficiency

Task-Day	Sample Type	Number of Replicates, by Spike Amount			
		250 µL Formulated Mixture	25 µL Formulated Mixture	Blank	Total Samples
4A - Aluminum Foil Elution Efficiency					
	Aluminum foil squares	7	7	2	16
	Extraction solvent spikes	2	2	2	6
4B - Handwipe Extraction Efficiency					
	Isopropanol handwipes	7	7	2	16
	Extraction solvent spikes	2	2	2	6
4C - Handwipe Removal Efficiency					
4C - Day 1					
	Aluminum foil squares	5	1	1	7
	Hand presses – subject A: L/R				
	subject B: L/R				
	Isopropanol handwipes	4+1	1	1	7
	Extraction solvent spikes	2	2	1	5
4C - Day 2					
	Aluminum foil squares	5	1	1	7
	Hand presses – subject A: L/R				
	subject B: L/R				
	Isopropanol handwipes	4+1	1	4+1	11
	Extraction solvent spikes	2	2	1	5
4C - Day 3					
	Aluminum foil squares	5	1	1	7
	Hand presses – subject A: L/R				
	subject B: L/R				
	Isopropanol handwipes	4+1	1	4+1	11
	Extraction solvent spikes	2	2	1	5
Total Samples		54	30	25	109

Table 16 Sampling Periods and Environmental Measurements Made During Transfer Sampling

Experiment	Day	Sampling Period: Date	Sampling Period: Time	Room Air: Mean Temp[a], °C	Room Air: Mean Relative Humidity[b], °C	Mean Carpet Temp, °C
1		8-4-92	1042-1229	30[c]	61[c]	
2		8-10-92	1048-1238	31[c]	58[c]	
3		11-24-92	1047-1231	20[c]	29[c]	
4C	1	3-3-93	1045-1055			
4C	2	3-17-93	1130-1136			
4C	3	3-24-93	1129-1142			
5A		3-2-93	1102-1255	18	54	
5B		3-9-93	1305-1401	27	40	
5C	1	3-16-93	1105-1158	23	62	
5C	2	3-25-93	1220-1303	24	66	
5E	1	4-20-93	1125-1220	22	61	
5E	2	4-27-93	1048-1145	22	65	
5D		5-19-93	1105-1222	27	50	
6A	1	6-16-93	1316-1410	22	58	
6A	2	6-17-93	1413-1452	23	54	
6A	3	6-18-93	1325-1502	23	53	
6B	1	6-22-93	1330-1416	22	56	
6B	2	6-23-93	1328-1411	22	61	
6B	3	6-24-93	1550-1639	22	60	
8A		7-23-93	Cool: 1044-1101	17		22
			Mod: 1316-1335	27	71	27
			Hot: 1614-1634	34	76	31
8B		7-29-93	Cool: 1125-1153	21	55	23
			Mod: 1329-1355	30	52	27
			Hot: 1607-1634	34	51	30
7	3	8-10-93	1541-1620	22	52	24[d]
7	4	8-11-93	1324-1403	22	49	23[d]
7	5	8-12-93	1323-1402	23	49	24[c]

a Collected 15 cm above floor
b Sling psychrometer, 1.5 m above floor
c Ambient (outdoor) conditions
d Sheet vinyl flooring temperature

Table 17. Isopropanol Handwipe Laboratory Blanks and Field Blanks[a] (μg/sample)

Exp-Day-Subj/Hand	Chlorpyrifos	Methoprene	Piperonyl Butoxide	Pyrethrin I
Lab Blanks: Isopropanol Sof-Wick® Gauze				
4C-1	<0.01	—	—	<0.05
4C-2	<0.01	—	—	<0.05
4C-3	<0.01	—	—	<0.05
Field Blanks: Single Hand Press onto Aluminum Foil/Isopropanol Handwipe				
4C-2-AR	0.38	—	—	<0.05
4C-2-BR	0.12	—	—	<0.05
4C-2-AL	0.23	—	—	<0.05
4C-2-BL	0.14	—	—	<0.05
4C-3-AL	0.10	—	—	<0.05
4C-3-BL	0.20	—	—	<0.05
4C-3-AR	0.11	—	—	<0.05
4C-3-BR	0.13	—	—	<0.05
Field Blanks: Single Hand Press onto Cleaned Carpet (48 cm^2)/Isopropanol Handwipe				
6A-0A-AR	0.60	<0.05	0.06[b]	<0.05
6A-0A-BR	0.26	<0.05	<0.05	<0.05
6A-0A-CR	0.45	<0.05	<0.05	<0.05
6A-0A-AL	0.24	<0.05	<0.05	<0.05
6A-0A-BL	0.25	<0.05	<0.05	<0.05
6A-0A-CL	0.19	<0.05	<0.05	<0.05
6A-0B-AR	0.15	<0.05	<0.05	<0.05
6A-0B-BR	0.16	<0.05	<0.05	<0.05
6A-0B-CR	0.14	<0.05	<0.05	<0.05
6A-0B-AL	0.22	<0.05	<0.05	<0.05
6A-0B-BL	0.26	<0.05	<0.05	<0.05
6A-0B-CL	0.15	<0.05	<0.05	<0.05
Field Blanks: Ten Hand Presses onto Clean Cardstock (480 cm^2)/Isopropanol Handwipe				
6B-0-AR	0.22	<0.05	<0.05	<0.05
6B-0-BR	0.22	<0.05	<0.05	<0.05
6B-0-CR	0.17	<0.05	<0.05	<0.05
6B-0-AL	0.13	<0.05	<0.05	<0.05
6B-0-BL	0.15	<0.05	<0.05	<0.05
6B-0-CL	0.11	<0.05	<0.05	<0.05
6B-4-AL	0.11	<0.03	0.03[b]	<0.02
6B-4-BL	0.19	<0.03	<0.03	<0.02
6B-4-CL	0.17	<0.03	INT[c]	<0.02
6B-4-AR	0.11	<0.03	<0.03	<0.02
6B-4-BR	0.16	<0.03	<0.03	<0.02
6B-4-CR	0.16	<0.03	INT	<0.02
7-1-AL	<0.20	<0.40	<0.45	<0.90
7-1-CL	0.25	<0.40	<0.45	<0.90
7-1-AR	0.23	<0.40	<0.45	<0.90
7-1-CR	0.24	<0.40	<0.45	<0.90

Table 17. Continued

Exp-Day-Subj Hand	Chlorpyrifos	Methoprene	Piperonyl Butoxide	Pyrethrin I
Field Blanks: Ten Hand Presses onto Clean Cardstock (480 cm²)/Isopropanol Handwipe (Cont'd)				
7-2-AR	0.88	<0.40	<0.45	<0.90
7-2-BR	0.25	<0.40	<0.45	<0.90
7-2-CR	0.24	<0.40	<0.45	<0.90
7-2-AL	0.27	<0.40	<0.45	<0.90
7-2-BL	0.31	<0.40	<0.45	<0.90
7-2-CL	0.24	<0.04	<0.45	<0.90

a All field blank hand presses were performed above (on, in Exp. 6A) the surface in the same room where hand press samples were collected on other days
b Present in solvent blank at similar level
c INT = Quantitation obscured by interference

Table 18. Field Spike Recoveries (%) from Alpha-cellulose Coupons

Experiment	Chlorpyrifos	Methoprene	Piperonyl Butoxide	Pyrethrin I
Range of spike amounts, µg	(527-3000)	(16.3-18.9)	(856-1430)	(33.5-114)
1-1	88			
1-2	71			
2-1	93			
2-2	98			
3-1	106			
3-2	110			
5A	103			
5B	95			
5C1	56[a]			
5C2	86			
5D	108			
5E1	118			
5E2	94			
6A	98		67	122
6B-2		108		160
6B-3		93		137
8B-1	92		69	102
8B-2	103		78	109
No. samples, n	16 (15)[a]	2	3	5
Mean, $\bar{x}$	94.9 (97.5)[a]	100.5	71.3	126.0
Std. dev., s	15.1 (11.4)[a]	10.6	5.9	23.2
Coef. of variation	0.159 (0.117)[a]	0.106	0.082	0.184

a Excludes apparent outlier

Table 19. Field Spike Recoveries (%) from Denim Drag Cloths

Experiment	Chlorpyrifos	Methoprene	Piperonyl Butoxide	Pyrethrin I
Range of spike amounts, μg	(0.24-500)	(0.04-0.17)	(5.1-88)	(0.31-0.68)
1-1	115			
1-2	88			
2-1	113			
2-2	208[a]			
3-1	98			
3-2	101			
5D-1	86			
5D-2	88			
5E1-1	133			
5E1-2	116			
5E2-1	104			
5E2-2	91			
6A-2	90		73	87
6A-3	97		76	118
6B-2	111	96		145
6B-3	116	120		ND[b,a]
7-5	82		115	105
8A-1	154[a]	153[a]		
8A-2	203[a]	132[a]		
8B-1	89		75	92
8B-2	93		76	121
No. samples, n	21 (18)[a]	4 (2)[a]	5	7 (6)[a]
Mean, x̄	113.1 (100.6)[a]	125.2 (108.0)[a]	83.0	95.4 (111.3)[a]
Std. dev., s	35.3 (13.9)[a]	23.8 (17.0)[a]	17.9	46.4 (21.3)[a]
Coef. of variation	0.312 (0.138)	0.190 (0.157)[a]	0.216	0.486 (0.192)[a]

a Excludes apparent outlier(s)
b ND = Not detected

Table 20. Field Spike Recoveries (%) from Dry PUF Rings

Experiment	Chlorpyrifos	Methoprene	Piperonyl Butoxide	Pyrethrin I
Range of spike amounts, µg	(0.24-500)	(0.04-0.17)	(5.1-8.8)	(0.31-0.68)
1-1	108			
1-2	34[a]			
2-1	117			
2-2	144			
3-1	107			
3-2	108			
5A-1	90			
5A-2	103			
5B-1	138			
5B-2	104			
5C1-1	101			
5C1-2	103			
5C2-1	77			
5C2-2	84			
6A-2	86		72	99
6A-3	89		73	91
6B-2	107	105		160
6B-3	93	96		133
7-3	98		118	104
7-5	100		105	143
8A-1	118	128		
8A-2	120	118		
8B-1	97		85	107
8B-2	97		84	101
No. samples, n	24 (23)[a]	4	6	8
Mean, $\bar{x}$	101.0 (103.9)[a]	111.8	89.5	117.2
Std. dev., s	21.1 (15.9)[a]	14.1	18.3	24.8
Coef. of variation	0.209 (0.153)[a]	0.126	0.205	0.212

a Excludes apparent outlier

Table 21. Field Spike Recoveries (%) from Isopropanol-moistened SOF-WICK® Gauze Handwipes

Experiment	Chlorpyrifos	Methoprene	Piperonyl Butoxide	Pyrethrin I
Range of spike amounts, μg	(0.95-25.2)	0.17	(4.5-7.4)	(0.31-319)
4B-L1	95			97
4B-L2	86			109
4B-L3	96			111
4B-L4	79			81
4B-L5	84			83
4B-L6	91			110
4B-L7	84			86
4B-H1	105			113
4B-H2	97			103
4B-H3	106			112
4B-H4	96			97
4B-H5	101			100
4B-H6	97			90
4B-H7	95			93
6A-2-1	69		70	122
6A-2-2	75		72	117
6A-3-1	79		78	98
6A-3-2	59		56	53
6B-2-1	54	58		84
6B-2-2	58	68		85
6B-3-1	70	87		99
6B-3-2	69	85		100
7-3-1	95		141	291[a]
7-3-2	101		150	155
7-5-1	86		167	228[a]
7-5-2	96		126	171
No. samples, n	26	4	8	26 (24)[a]
Mean, $\bar{x}$	85.5	74.5	107.5	114.9 (102.9)[a]
Std. dev., s	14.9	13.9	43.1	49.1 (23.7)[a]
Coef. of variation	0.175	0.187	0.401	0.427 (0.231)[a]

a Excludes apparent outliers

Table 22. Spike Recoveries (%) from Aluminum Foil Squares[a]

Experiment 4A Replicate	Chlorpyrifos	Pyrethrin I
Low Spike Amount[b]	1.86 μg	17.5 μg
4A-L1	137	153
4A-L2	119	122
4A-L3	90	94
4A-L4	108	101
4A-L5	99	88
4A-L6	92	80
4A-L7	90	84
n	7	7
$\bar{x}$	105	103
s	18	26
High Spike Amount[b]	23.9 μg	246. μg
4A-H1	107	116
4A-H2	110	112
4A-H3	100	106
4A-H4	91	89
4A-H5	95	95
4A-H6	92	87
4A-H7	104	95
n	7	7
$\bar{x}$	100	100
s	7	11

a Spiked formulated mixture allowed to dry on foil before extraction

b Spiked amount determined from the mean of the analysis of three replicates each of two solvent spikes

Table 23. Comparison of Transfers of Chlorpyrifos Residues from Plush Nylon Carpet in Experiment 1 by Cloth Roller, Drag Sled, and PUF Roller[a]

		Deposition		Cloth Roller		Drag Sled		PUF Roller	
Block	Sampled Direction[b]	Coupon Amount µg	Surface Loading ng/cm^2	Transfer Amount µg	Transfer Rate ng/cm^2	Transfer Amount µg	Transfer Rate ng/cm^2	Transfer Amount µg	Transfer Rate ng/cm^2
I	A/W	2,960	28,800	1,110	605	182	196	106	140
II	A/W	660	6,400	1,430	775	138	148	79	104
III	X	750	7,300	780	424	165	177	81	106
IV	X	1,560	15,200	820	443	149	160	96	126
V	A/W	1,390	13,500	1,450	786	218	234	70	92
VI	A/W	990	9,600	1,760	958	161	173	131	172
No. samples, n			6		6		6		6
Mean, $\bar{x}$			13,470		665		181.3		123.2
Std. dev., s			8,240		211		30.5		29.4
Coef. of variation			0.61		0.32		0.17		0.24

a Sampled carpet area, number of passes, and pressure as defined in Table 1

b Direction relative to lay of carpet pile: A – against, W – with, X – across

Table 24. **Comparison of Transfers of Chlorpyrifos Residues from Level-loop Polypropylene Carpet in Experiment 2 by Cloth Roller, Drag Sled, and PUF Roller[a]**

Block	Sampled Direction[b]	Deposition		Cloth Roller		Drag Sled		PUF Roller	
		Coupon Amount µg	Surface Loading ng/cm^2	Transfer Amount µg	Transfer Rate ng/cm^2	Transfer Amount µg	Transfer Rate ng/cm^2	Transfer Amount µg	Transfer Rate ng/cm^2
I	A/W	1,220	11,800	750	408	113	122	150	197
II	A/W	970	9,400	410	224	114	123	90	118
III	X	1,000	11,700	880	476	138	148	134	176
IV	X	950	11,500	530	290	202	217	80	105
V	A/W	1,210	9,800	280	154	285	306	83	109
VI	A/W	1,180	9,200	340	183	127	137	201	264
No. samples, n			6		6		6		6
Mean, $\bar{x}$			10,570		289		175.5		161.5
Std. dev., s			1,230		129		73.0		63.0
Coef. of variation			0.12		0.45		0.42		0.39

a Sampled carpet area, number of passes, and pressure as defined in Table 1
b Direction relative to lay of carpet pile: A – against, W – with, X – across

Table 25. Comparison of Transfers of Chlorpyrifos Residues from Plush Nylon Carpet in Experiment 3 by the Drag Sled and PUF Roller Using Dry and Moistened Contact Media[a]

				Dry Contact Medium (Standard)				Moistened Contact Medium			
		Deposition		Drag Sled		PUF Roller		Drag Sled		PUF Roller	
Block	Sampled Direction[b]	Coupon Amount µg	Surface Loading ng/cm²	Transfer Amount µg	Transfer Rate ng/cm²	Transfer Amount µg	Transfer Rate ng/cm²	Transfer Amount µg	Transfer Rate ng/cm²	Transfer Amount µg	Transfer Rate ng/cm²
I	A/W	4,490	21,800	—[c]	—	—	—	152	164	47	62
II	X	4,810	23,400	45	48	34	45	53	57	434	572
III	X	4,370	21,200	80	86	47	62	90	96	505[d]	580[d]
IV	A/W	3,260	15,800	58	63	39	51	261	281	397	522
V	A/W	3,460	16,800	116	125	37	49	54	59	281	370
No. samples, n			5		4		4		5		5
Mean, $\bar{x}$			19,800		80.4		51.6		131		421
Std. dev., s			3,300		33.3		7.3		94		218
Coef. of variation			0.17		0.41		0.14		0.72		0.52

a Sampled carpet area, number of passes, and pressure as defined in Table 1
b Direction relative to lay of carpet pile: A – against, W – with, X – across
c No data since no sample planned
d Carpet area sampled was 870 cm²

Table 26. Observations from Field Use of Dislodgeable Residue Methods

Strengths	Weaknesses
Cloth Roller	
• Simple in design • Inexpensive to build from available materials	• Sampling cloth tends to bind and shift from original position • Plastic bag cover may adhere to PUF sleeve on roller from static • Difficult to operate due to mass of roller • Operator must contact treated surface • Susceptible to added pressure from operator • Transfer affected by roll orientation relative to lay of carpet fibers
Drag Sled	
• Simple in design • Inexpensive to build from available materials • Simple to use	• Drag contact unlike most skin contact with carpet • Drag contact is potentially directional relative to lay of carpet fibers
PUF Roller	
• Consistent use across operators due to few variables • Relatively simple to use • Foam roller contact is more like skin contact	• Expensive to build or purchase

Table 27. Experiment 5A: Effect of Number of Passes[a] of PUF Roller Sampler on Transfer of Fresh Chlorpyrifos Residue from Plush Carpet

Number of Passes[a]	Replicate Sampler Direction[b]	Transfer Amount, µg				Coefficient of Variation	Mean Transfer Rate µg/pass
		Crude	Adjusted	Mean	Std. Dev.		
1	A	5.7	4.4	9.9	6.6	0.67	9.9
	W	18.6	17.3				
	X	9.1	7.9				
2	A	46.6	45.3	26.2	17.8	0.68	13.1
	W	11.4	10.1				
	X	24.5	23.2				
4	A	26.4	25.1	48.5	20.9	0.43	12.1
	W	66.4	65.1				
	X	56.7	55.4				
8	A	52.9	51.6	76.8	22.2	0.29	9.6
	W	86.5	85.2				
	X	94.8	93.5				
20	A	128	127	172	90	0.52	8.6
	W	114	113				
	X	276	275				

a Repeat passes over 1.0 m strip of treated carpet
b Direction relative to lay of carpet pile: A – against, W -- with, X – across
c Adjusted transfer = crude transfer – mean stationary (3 s) transfer (determined in Exp. 5C) = crude transfer - 1.27 µg

Table 28. Experiment 5B. Effect of Pressure and Speed of PUF Roller Sampler on Transfer of Fresh Chlorpyrifos Residue from Plush Carpet[a]

PUF Roller			Transfer Amount, µg			Coefficient of Variation
Applied Pressure Pa	Speed m/s	Replicate Sampler Direction[b]	Amount	Mean	Std. Dev.	
2,400 (0.35 psi)	0.1	A	8.9	8.0	1.4	0.18
		W	6.4			
		X	8.8			
7,300 (1.05 psi)	0.1	A	32.6	26.8	5.2	0.19
		W	25.5			
		X	22.4			
18,000 (2.6 psi)	0.1	A	65.4	46.6	17.8	0.38
		W	29.9			
		X	44.6			
7,300 (1.05 psi)	0.3	A	23.6	21.4	5.8	0.27
		W	25.8			
		X	14.9			

a Single pass over 1 m length of carpet
b Direction relative to lay of carpet pile: A – against, W – with, X – across

Table 29. Experiment 5C: Effect of Carpet Length Traversed by PUF Roller Sampler[a] on Transfer of Fresh Chlorpyrifos Residue from Plush Carpet

PUF Roller Traverse Length	Replicate Day-Direction[b]	Transfer Amount, µg				Coefficient of Variation	Mean Transfer Rate µg/m
		Crude	Adjusted[c]	Mean	Std. Dev.		
0.0 m (stationary for 3 s)	1-W	0.89					
	1-X	1.10					
	2-W	2.03					
	2-X	1.05					
0.25 m	1-A	2.38	1.11	2.1	1.4	0.65	8.4
	1-W	4.18	2.91				
	2-A	2.08	0.81				
	2-W	4.91	3.64				
1.0 m	1-A	18.3	17.0	11.4	4.9	0.43	11.4
	1-W	9.8	8.5				
	2-A	—[d]	—				
	2-W	9.9	8.6				
3.0 m	1-A	48.6	47.3	57.2	8.3	0.14	19.0
	1-W	56.9	55.6				
	2-A	59.6	58.3				
	2-W	68.8	67.5				
10.0 m	1-W	103.3	102.0	79	33	0.41	7.9
	2-W	57.0	55.7				

a Single pass at normal pressure (7,300 Pa) and speed (0.1 m/s)

b Half experiment performed on each of two days. Direction relative to lay of carpet pile: A – against, W – with, X – across

c Adjusted transfer = crude transfer – mean stationary (3 s) transfer (determined for 0.0 m) = crude transfer - 1.27 µg

d Lost during extraction

Table 30. Experiment 5D: Effect of Pressure and Speed of Drag Sled Sampler on Transfer of Fresh Chlorpyrifos Residue from Plush Carpet[a]

Drag Sled						
Applied Pressure Pa	Speed m/s	Replicate Sampler Direction[b]	Transfer Amount, μg/m			Coefficient of Variation
			Amount	Mean	Std. Dev.	
2,100	0.07	A	22	36.3	12.7	0.35
		W	46			
		X	41			
4,500	0.07	A	86	55.7	27.6	0.50
		W	32			
		X	49			
15,600	0.07	A	45	43.3	9.6	0.22
		W	33			
		X	52			
4,500	0.2	A	24	30.7	20.8	0.68
		W	54			
		X	14			

a Single pass over 1 m length of carpet
b Direction relative to lay of carpet pile: A – against, W – with, X – across

Table 31: Experiment 5E. Effect of Carpet Length Traversed by Drag Sled Sampler[a] on Transfer of Fresh Chlorpyrifos Residue from Plush Carpet

Drag Sled Traverse Length	Replicate Day-Direction[b]	Transfer Amount, µg				Coefficient of Variation	Mean Transfer Rate µg/pass
		Crude	Adjusted[c]	Mean	Std. Dev.		
0.0 m (stationary for 3 s)	1-W	0.88					
	1-X	0.53					
	2-W	0.22					
	2-X	0.90					
0.17 m	1-A	5.1	4.5	4.2	0.6	0.13	24.8
	1-W	4.1	3.5				
	2-A	4.7	4.1				
	2-W	5.4	4.8				
0.92 m	1-A	8.1	7.5	8.6	2.0	0.24	9.4
	1-W	6.9	6.3				
	2-A	10.8	10.2				
	2-W	11.0	10.4				
2.92 m	1-A	52	52	124	68	0.55	42.4
	1-W	216	215				
	2-A	110	109				
	2-W	120	119				
9.76 m	1-W	266	265	302	52	0.17	31.0
	2-W	340	339				

a Single pass at normal pressure (4,500 Pa) and speed (0.07 m/s)

b Half experiment performed on each of two days. Direction relative to lay of carpet pile: A – against, W – with, X – across

c Adjusted transfer = crude transfer – mean stationary (3 s) transfer (determined for 0.0 m) = crude transfer - 0.63 µg

Table 32. Effect of Temperature on Transfer of Aged Chlorpyrifos Residues from Plush Carpet by the Drag Sled and PUF Roller in Experiment 8A[a]

Temp. Condition (Block)	Mean Temperature, °C		Room Air Concentration µg/m³	Sampled Direction[b]	Transfer Amount, µg	
	Air	Carpet			Drag Sled	PUF Roller
Cool	17	22	4.3	A	0.37	0.49
				W	0.50	0.29
				X	0.50	0.50
				x̄	0.46	0.43
				s	0.08	0.12
Moderate	27	27		A	1.09	0.74
				W	0.85	0.10
				X	0.98	0.74
				x̄	0.97	0.53
				s	0.12	0.37
Hot	34	31	9.5	A	0.98	1.04
				W	1.22	0.53
				X	0.95	0.76
				x̄	1.05	0.78
				s	0.14	0.25

a Single pass over 1 m strip of carpet as described in Table 2
b Direction relative to lay of carpet pile. A – against, W – with, X – across

Table 33. Effect of Temperature on Transfer of Aged Piperonyl Butoxide Residues from Plush Carpet by the Drag Sled and PUF Roller in Experiment 8A[a]

Temp. Condition (Block)	Mean Temperature, °C		Room Air Concentration µg/m³	Sampled Direction[b]	Transfer Amount, µg	
	Air	Carpet			Drag Sled	PUF Roller
Cool	17	22	0.17	A	2.5	3.4
				W	1.7	2.9
				X	3.3	2.8
				$\bar{x}$	2.5	3.0
				s	0.8	0.3
Moderate	27	27		A	5.9	4.8
				W	8.0	0.8
				X	3.9	2.6
				$\bar{x}$	5.9	2.7
				s	2.0	2.0
Hot	34	31	0.40	A	6.5	5.0
				W	5.5	2.1
				X	2.4	3.5
				$\bar{x}$	4.8	3.6
				s	2.1	1.4

a Single pass over 1 m strip of carpet as described in Table 2
b Direction relative to lay of carpet pile: A – against, W – with, X – across

Table 34. Effect of Temperature on Transfer of Aged Pyrethrin I Residues from Plush Carpet by the Drag Sled and PUF Roller in Experiment 8A[a]

Temp. Condition (Block)	Mean Temperature, °C		Room Air Concentration µg/m³	Sampled Direction[b]	Transfer Amount, µg	
	Air	Carpet			Drag Sled	PUF Roller
Cool	17	22	<0.05	A	0.17	0.30
				W	0.44	0.42
				X	0.22	0.33
				$\bar{x}$	0.28	0.35
				s	0.14	0.06
Moderate	27	27		A	0.49	0.64
				W	0.59	0.05
				X	0.29	0.17
				$\bar{x}$	0.46	0.41
				s	0.16	0.33
Hot	34	31	<0.3	A	0.56	0.44
				W	0.31	0.24
				X	0.36	0.26
				$\bar{x}$	0.41	0.31
				s	0.13	0.11

a Single pass over 1 m strip of carpet as described in Table 2
b Direction relative to lay of carpet pile: A – against, W – with, X – across

Table 35. Effect of Temperature on Transfer of Fresh Chlorpyrifos Residues from Plush Carpet by the Drag Sled and PUF Roller in Experiment 8H[a]

Temp. Condition Block	Mean Temperature, °C: Air	Mean Temperature, °C: Carpet	Room Air Concentration µg/m³	Deposition: Coupon Amount µg	Deposition: Relative Coupon Mean[c]	Sampled Direction[b]	Drag Sled Transfer, µg: Amount	Drag Sled Transfer, µg: Coupon Adjustment[d]	PUF Roller Transfer, µg: Amount	PUF Roller Transfer, µg: Coupon Adjustment[d]
Cool	21	23	6.3			A	8.1		5.7	
NE				720		W	8.9		2.6	
NW				1,400		X	13.9		5.7	
Mean, x̄				1,060	0.92		10.3	11.2	4.7	5.1
Std. dev., s				480			3.1		1.8	
Moderate	30	27				A	11.7		4.5	
CE				1,530		W	30.9		6.9	
CW				1,410		X	13.5		9.3	
Mean, x̄				1,470	1.27		18.7	14.7	6.9	5.4
Std. dev., s				80			10.6		2.4	
Hot	34	30	27.8			A	9.8		6.3	
SE				830		W	6.6		4.8	
SW				1,030		X	16.6		5.5	
Mean, x̄				930	0.81		11.0	13.6	5.5	6.9
Std. dev., s				140			5.1		0.8	

a Single pass over 1 m strip of carpet as described in Table 2
b Direction relative to lay of carpet pile: A – against, W – with, X – across
c $\bar{x}/(\sum \bar{x}/n)$
d Transfer mean/relative coupon mean

Table 36. Effect of Temperature on Transfer of Fresh Piperonyl Butoxide Residues from Plush Carpet by the Drag Sled and PUF Roller in Experiment 81[a]

Temp. Condition Block	Mean Temperature, °C		Room Air Concentration μg/m³	Deposition		Sampled Direction[b]	Drag Sled Transfer, μg		PUF Roller Transfer, μg	
	Air	Carpet		Coupon Amount μg	Relative Coupon Mean[c]		Amount	Coupon Adjustment[d]	Amount	Coupon Adjustment[d]
Cool	21	23	0.10			A	11.0		7.8	
NE				570		W	12.2		3.8	
NW				1,200		X	19.7		7.5	
Mean, x̄				890	0.95		14.3	15.0	6.4	6.7
Std. dev., s				440			4.7		2.2	
Moderate	30	27				A	17.8		5.2	
CE				1,190		W	41.0		8.0	
CW				1,180		X	22.5		10.6	
Mean, x̄				1,180	1.27		27.1	21.3	7.9	6.2
Std. dev., s				10			12.3		2.7	
Hot	34	30	0.44			A	15.5		8.2	
SE				640		W	10.9		6.4	
SW				800		X	25.2		6.9	
Mean, x̄				720	0.78		17.2	22.1	7.1	9.2
Std. dev., s				120			7.3		0.9	

a Single pass over 1 m strip of carpet as described in Table 2
b Direction relative to lay of carpet pile: A – against, W – with, X – across
c $\bar{x}/(\sum \bar{x}/n)$
d Transfer mean/relative coupon mean

Table 37. Effect of Temperature on Transfer of Fresh Pyrethrin I Residues from Plush Carpet by the Drag Sled and PUF Roller in Experiment 8I[a]

Temp. Condition Block	Mean Temperature, °C		Room Air Concentration µg/m³	Deposition		Sampled Direction[b]	Drag Sled Transfer, µg		PUF Roller Transfer, µg	
	Air	Carpet		Coupon Amount µg	Relative Coupon Mean[c]		Amount	Coupon Adjustment[d]	Amount	Coupon Adjustment[d]
Cool	21	23	0.18			A	1.50		0.74	
NE				78		W	1.49		0.40	
NW				191		X	2.02		0.83	
Mean, x̄				134	0.96		1.67	1.75	0.66	0.69
Std. dev., s				80			0.30		0.23	
Moderate	30	27				A	1.80		0.58	
CE				167		W	4.75		1.00	
CW				157		X	2.68		1.08	
Mean, x̄				162	1.15		3.08	2.67	0.89	0.77
Std. dev., s				8			1.51		0.27	
Hot	34	30	0.09			A	2.69		1.18	
SE				111		W	1.39		0.74	
SW				140		X	3.46		0.90	
Mean, x̄				125	0.89		2.51	2.82	0.94	1.06
Std. dev., s				20			1.05		0.23	

a Single pass over 1 m strip of carpet as described in Table 2
b Direction relative to lay of carpet pile: A – against, W – with, X – across
c $\bar{x}/(\sum \bar{x}/n)$
d Transfer mean/relative coupon mean

Table 38. Reduction in Chlorpyrifos Transfer from Plush Carpet[a] Using the Drag Sled and PUF Roller with Time after Application

Experiment	Date of Application	Days After Application	Drag Sled Transfer Mean µg	Drag Sled Transfer Relative Transfer	PUF Roller Transfer Mean µg	PUF Roller Transfer Relative Transfer
3	11-24-92	0	75	1.00	39[b]	1.00
		93	0.27	0.004	0.56[b]	0.014
5A	3-2-93	0			27.5[b]	1.00
		3			7.0[b]	0.25
5B	3-9-93	0			26.8	1.00
		3			4.2	0.16
5C1	3-16-93	0			14.0	1.00
		6			3.0	0.22
5C2	3-25-93	0			9.9	1.00
		15			2.6	0.26
5E1	4-20-93	0	7.5	1.00		
		3	4.5	0.60		
5E2	4-27-93	0	10.9	1.00		
		17	0.62	0.06		
5D	5-19-93	0	55.7	1.00		
		23	1.02	0.018		
6A	6-16-93	0	7.1	1.00	2.12	1.00
		1	2.2	0.30	0.97	0.46
		2	3.5	0.49	1.09	0.52
		6	1.7	0.24	1.03	0.49
		6[c]	6.8	0.96	2.24	1.06
		7	9.2	1.28	2.31	1.09
		8	5.0	0.69	2.66	1.26
		31			0.53	0.25
		37	0.46	0.06	0.43	0.20
		43	0.63	0.09	0.52	0.24

a Single pass over 1 m strip of carpet
b Two passes over 1 m strip of carpet
c Aerosol can application of methoprene/pyrethrins/piperonyl butoxide formulation

Table 39. Reduction in Piperonyl Butoxide Transfer from Plush Carpet Using the Drag Sled and PUF Roller with Time after Application

Experiment	Date of Application	Days After Application	Drag Sled Transfer Mean µg	Drag Sled Transfer Relative Transfer	PUF Roller Transfer Mean µg	PUF Roller Transfer Relative Transfer
6A	6-16-93	0	8.1	1.00	2.3	1.00
		1	3.0	0.38	1.2	0.53
		2	4.9	0.61	1.4	0.61
		6	2.4	0.30	1.1	0.48
6B	6-22-93	0	131	1.00	54	1.00
		1	105	0.80	34	0.63
		2	55.6	0.42	44	0.81
		25			4.3	0.08
		31	2.5	0.019	3.0	0.06
		37	2.4	0.018	2.3	0.04

Table 40. Reduction in Pyrethrin I Transfer from Plush Carpet Using the Drag Sled and PUF Roller with Time after Application

			Drag Sled Transfer		PUF Roller Transfer	
Experiment	Date of Application	Days After Application	Mean µg	Relative Transfer	Mean µg	Relative Transfer
6A	6-16-93	0	1.39	1.00	0.26	1.00
		1	0.43	0.31	0.15	0.59
		2	0.54	0.39	0.12	0.46
		6	0.45	0.32	0.18	0.67
6B	6-22-93	0	40.9	1.00	13.8	1.00
		1	38.0	0.93	9.9	0.72
		2	7.2	0.18	12.8	0.92
		25			0.29	0.021
		31	0.28	0.007	0.35	0.025
		37	0.17	0.004	0.17	0.013

Table 41. Reduction in Chlorpyrifos Transfer[a] from Used Plush Nylon Carpet After Commercial Cleaning by Water Extraction[b]

Date Carpet Cleaned[b]	Experiment Performed After Cleaning	Mean Transfer (µg) by Method: Drag Sled, Before Cleaning	Drag Sled, After Cleaning	PUF Roller, Before Cleaning	PUF Roller, After Cleaning
2-25-93	5A	0.3[c]	0.05[c]	0.6[d]	0.1[d]
3-5-93	5B			7.0[d]	0.4[d]
3-12-93	5C1			4.2	1.0
3-22-93	5C2			3.5	1.6
4-9-93	5E1	0.7	0.8		
4-23-93	5E2	4.6	1.0		
5-14-93	5D	0.6	1.5		
6-11-93	6A	1.0	1.2	0.7	0.8

a Single pass over 1 m strip of carpet
b Cleaning consisted of application of a spot cleaner to remove marks, extraction using a chemical carpet cleaner, rinsing with clean water, and drying for 48 hours with rapid air ventillation
c Pass over 4 ft strip
d Two passes over 1 m strip

Table 42. Elution Efficiency from Aluminum Foil Squares and Extraction Efficiency from Isopropanol-moistened Gauze Wipes for Chlorpyrifos and Pyrethrin I in Experiment 4

Experiment	Spiked Analyte	Spike Level	Spiked Amount[a] µg	No. of Replicates n	Recovery, % Mean	Std. Dev.	Coefficient of Variation
4A: Elution Efficiency from Aluminum Foil Squares[b]							
	Chlorpyrifos	Low	1.86	7	105.1	17.7	0.168
		High	23.9	7	99.9	7.2	0.072
	Pyrethrin I	Low	17.5	7	103.2	26.1	0.253
		High	246.	7	99.9	11.3	0.113
4B Extraction Efficiency from Isopropanol-moistened Sof-Wick® Gauze Handwipes							
	Chlorpyrifos	Low	1.93	7	87.8	6.2	0.071
		High	25.2	7	99.7	4.5	0.045
	Pyrethrin I	Low	16.1	7	96.9	13.6	0.140
		High	319.	7	101.1	8.8	0.087

a Spiked amount was determined from the mean of the analysis of three replicates each of two solvent spikes
b Spiked formulated mixture was allowed to dry on foil before extraction

Table 43 Wipe[a] Removal Efficiency of Chlorpyrifos Residue from the Human Hand by the Isopropanol Handwipe Method in Experiment 4C

Date	Subject Hand	Amount, µg: Spiked onto Foil[b]	Left on Foil after Hand Press[c]	Transferred to Hand	Removed by Handwipe[d]	Removal Efficiency %
3-3-93	AL	4.32	0.63	3.69	3.14	85.2
	BL	4.32	0.78	3.54	3.17	89.4
	AR	4.32	0.25	4.07	4.19	103.0
	BR	4.32	0.26	4.06	4.11	101.3
3-17-93	AR	4.20	0.84	3.36	3.53	105.1
	BR	4.20	0.97	3.23	3.59	111.1
	AL	4.20	0.24	3.96	4.69	118.5
	BL	4.20	0.58	3.62	3.52	97.2
3-24-93	AL	4.26	0.56	3.70	4.24	114.5
	BL	4.26	0.90	3.36	3.29	98.0
	AR	4.26	0.15	4.11	4.81	116.9
	BR	4.26	0.70	3.56	3.97	111.7
No replicates, n						12
Removal efficiency mean						104.3
Removal efficiency std dev						10.7
Coefficient of variation						0.102

a Wipe performed within one minute after hand press into dried residue on aluminum foil
b Spiked amount was determined from the mean of the analysis of three replicates each of two solvent spikes
c Corrected for mean elution efficiency of 105.1% = $M_{foil}/1.051$
d Corrected for mean handwipe field blank of 0.18 µg and for mean isopropanol SOF-WICK® gauze extraction efficiency of 87.8% during Experiment 4 = $(M_{wipe} - 0.18\ \mu g)/0.878$

Table 44. Wipe[a] Removal Efficiency of Pyrethrin I Residue from the Human Hand by the Isopropanol Handwipe Method in Experiment 4C

Date	Subject Hand	Amount, µg: Spiked onto Foil[b]	Left on Foil after Hand Press[c]	Transferred to Hand	Removed by Handwipe[d]	Removal Efficiency %
3-3-93	AL	40.5	6.4	34.1	19.0	55.6
	BL	40.5	7.6	32.8	20.7	63.0
	AR	40.5	4.1	36.4	24.6	67.6
	BR	40.5	2.9	37.5	25.7	68.4
3-17-93	AR	51.1	13.1	38.0	29.2	76.7
	BR	51.1	14.8	36.3	36.8	101.2
	AL	51.1	3.4	47.7	43.8	91.9
	BL	51.1	7.4	43.8	38.0	86.8
3-24-93	AL	44.8	8.6	36.2	46.2	127.7
	BL	44.8	10.4	34.4	40.0	116.1
	AR	44.8	2.5	42.2	43.1	102.0
	BR	44.8	11.5	33.3	48.1	144.4
No. replicates, n						12
Removal efficiency mean						91.8
Removal efficiency std. dev.						27.6
Coefficient of variation						0.300

a Wipe performed within one minute after hand press into dried residue on aluminum foil

b Spiked amount was determined from the mean of the analysis of three replicates each of two solvent spikes

c Corrected for mean elution efficiency of 103.2% = $M_{foil}/1.032$

d Corrected for mean isopropanol SOF-WICK® gauze extraction efficiency of 96.9% during Experiment 4 = $(M_{wipe} - 0.0\ \mu g)/0.969$

Table 45. Comparison of Transfers of Chlorpyrifos Residues from Plush Carpet in Experiment 6A by Drag Sled, PUF Roller, and Human Hand Press

	Deposition		Drag Sled		PUF Roller		Human Hand Press	
Block	Coupon Amount µg	Surface Loading ng/cm²	Transfer Amount µg	Transfer Rate ng/cm²	Transfer Amount µg	Transfer Rate ng/cm²	Subject Hand	Net Transfer Amount[a] µg
6-16-93 (Application)								
NE	1,240	6,020	8.49	11.17	1.60	2.10	AR	LB[b]
							BR	0.03
							CR	LB
NW	970	4,680	5.77	7.60	2.64	3.47	AL	LB
							BL	LB
							CL	0.06
6-17-93								
CE	1,510	7,320	1.80	2.37	1.26	1.66	AL	___[c]
							BL	LB
							CL	LB
CW	1,360	6,590	2.51	3.30	0.68	0.89	AR	LB
							BR	LB
							CR	0.04
6-18-93								
SE	940	4,530	3.66	4.82	0.68	0.90	AR	LB
							BR	LB
							CR	LB
SW	1,200	5,790	3.31	4.35	1.50	1.98	AL	___[c]
							BL	LB
							CL	LB
No. samples, n		6		6		6		
Mean, $\bar{x}$		5,820		5.60		1.83		
Std. dev., s		1,080		3.25		0.96		
Coef. of variation		0.19		0.58		0.52		

a Net amount = Crude handwipe amount - mean handwipe background = X - 0.26 µg
b LB = crude amount is less than background amount
c Sample lost

Table 46. Comparison of Transfers of Piperonyl Butoxide Residues from Plush Carpet in Experiment 6A by Drag Sled, PUF Roller, and Human Hand Press

	Deposition		Drag Sled		PUF Roller		Human Hand Press	
Block	Coupon Amount µg	Surface Loading ng/cm²	Transfer Amount µg	Transfer Rate ng/cm²	Transfer Amount µg	Transfer Rate ng/cm²	Subject Hand	Net Transfer Amount[a] µg
6-16-93 (Application)								
NE	1,240	6,020	11.19	14.72	1.64	2.15	AR	0.14
							BR	<0.2
							CR	<0.2
NW	960	4,670	4.96	6.53	3.04	4.00	AL	0.07
							BL	<0.2
							CL	<0.2
6-17-93								
CE	1,520	7,370	2.83	3.72	1.64	2.16	AL	—[b]
							BL	<0.05
							CL	0.08
CW	1,380	6,660	3.25	4.28	0.82	1.08	AR	<0.05
							BR	<0.05
							CR	0.06
6-18-93								
SE	810	3,940	5.52	7.26	0.71	0.94	AR	<0.03
							BR	<0.03
							CR	<0.03
SW	1,220	5,920	4.27	5.62	2.13	2.81	AL	—[b]
							BL	<0.03
							CL	<0.03
No. samples, n		6		6		6		
Mean, x̄		5,760		7.02		2.19		
Std. dev., s		1,260		4.00		1.14		
Coef. of variation		0.22		0.57		0.52		

a Since handwipe field blank amounts were <0.05 µg, no background is subtracted
b Sample lost

Table 47. Comparison of Transfers of Pyrethrin I Residues from Plush Carpet in Experiment 6A by Drag Sled, PUF Roller, and Human Hand Press

Block	Deposition		Drag Sled		PUF Roller		Human Hand Press	
	Coupon Amount µg	Surface Loading ng/cm²	Transfer Amount µg	Transfer Rate ng/cm²	Transfer Amount µg	Transfer Rate ng/cm²	Subject Hand	Net Transfer Amount[a] µg
6-16-93 (Application)								
NE	197	954	2.12	2.79	0.187	0.25	AR	<0.2
							BR	INT[b]
							CR	<0.2
NW	152	736	0.66	0.87	0.336	0.44	AL	<0.2
							BL	INT
							CL	<0.2
6-17-93								
CE	153	741	0.36	0.48	0.194	0.26	AL	—[c]
							BL	INT
							CL	<0.05
CW	100	484	0.50	0.65	0.113	0.15	AR	INT
							BR	INT
							CR	INT
6-18-93								
SE	29	140	0.55	0.73	0.072	0.10	AR	<0.05
							BR	<0.05
							CR	<0.05
SW	56	274	0.54	0.71	0.167	0.22	AL	—[c]
							BL	<0.05
							CL	<0.05
No. samples, n		6		6		6		
Mean, x̄		555		1.04		0.23		
Std. dev., s		311		0.87		0.12		
Coef. of variation		0.56		0.84		0.51		

a Since handwipe field blank amounts were <0.05, no background is subtracted
b INT = Elevated background due to interference
c Sample lost

Table 48. Comparison of Transfers of Chlorpyrifos Residues[a] from Plush Carpet in Experiment 6B by Drag Sled, PUF Roller, and Human Hand Press

Block	Deposition[a]		Drag Sled		PUF Roller		Human Hand Press		
	Coupon Amount µg	Surface Loading ng/cm²	Transfer Amount µg	Transfer Rate ng/cm²	Transfer Amount µg	Transfer Rate ng/cm²	Subject Hand	Net Transfer Amount[b] µg	Transfer Rate ng/cm²
6-22-93									
NE			7.84	10.32	2.03	2.67	AR	0.22	0.45
							BR	0.49	1.03
							CR	0.20	0.42
NW			5.80	7.63	2.45	3.22	AL	0.38	0.80
							BL	0.83	1.73
							CL	0.22	0.45
6-23-93									
CE			11.35	14.94	2.50	3.29	AL	1.24	2.58
							BL	0.51	1.06
							CL	0.87	1.82
CW			6.97	9.18	2.11	2.78	AR	1.07	2.23
							BR	0.95	1.98
							CR	1.28	2.66
6-24-93									
SE			7.31	9.61	2.04	2.69	AR	0.46	0.97
							BR	0.74	1.54
							CR	0.52	1.09
SW			2.60	3.42	3.27	4.30	AL	0.31	0.64
							BL	0.09	0.18
							CL	0.73	1.53
No. samples, n				6		6			18
Mean, $\bar{x}$				9.18		2.93			1.29
Std. dev., s				3.75		0.30			0.76
Coef. of variation				0.41		0.10			0.59

a No chlorpyrifos was applied for Experiment 6B, but chlorpyrifos had been applied on 6-16-93 for Experiment 6A

b Net amount = crude handwipe amount - mean handwipe background = X - 0.16 µg

Table 49. Comparison of Transfers of Methoprene Residues[a] from Plush Carpet in Experiment 6B by Drag Sled, PUF Roller, and Human Hand Press

Block	Deposition: Coupon Amount µg	Deposition: Surface Loading ng/cm^2	Drag Sled: Transfer Amount µg	Drag Sled: Transfer Rate ng/cm^2	PUF Roller: Transfer Amount µg	PUF Roller: Transfer Rate ng/cm^2	Human Hand Press: Subject Hand	Human Hand Press: Net Transfer Amount[a] µg	Human Hand Press: Transfer Rate ng/cm^2
6-22-93 (Application)									
NE	20.0	96.7	2.25	2.96	0.92	1.20	AR	0.09	0.18
							BR	0.19	0.39
							CR	0.13	0.27
NW	24.2	117.0	2.45	3.22	0.92	1.20	AL	0.30	0.63
							BL	0.45	0.93
							CL	0.23	0.48
6-23-93									
CE	13.0	62.9	1.71	2.25	0.28	0.36	AL	0.15	0.32
							BL	0.06	0.13
							CL	0.06	0.13
CW	11.6	56.1	1.23	1.62	0.37	0.49	AR	0.10	0.21
							BR	0.10	0.22
							CR	0.10	0.22
6-24-93									
SE	16.8	81.3[b]	0.13	0.17[b]	0.41	0.53[b]	AR	<0.05	<0.11[b]
							BR	<0.05	<0.11[b]
							CR	<0.05	<0.11[b]
SW	16.8	81.4[b]	0.15	0.20[b]	0.32	0.42[b]	AL	<0.05	<0.11[b]
							BL	<0.05	<0.11[b]
							CL	<0.05	<0.11[b]
No. samples, n		4[b]		4[b]		4[b]			12[b]
Mean, $\bar{x}$		83.2[b]		2.51[b]		0.82[b]			0.34[b]
Std. dev., s		28.7[b]		0.72[b]		0.45[b]			0.24[b]
Coef. of variation		0.34[b]		0.29[b]		0.56[b]			0.70[b]

a Since handwipe field blank amounts were <0.03 µg, no background is subtracted

b Excluded from summary statistics

Table 50. Comparison of Transfers of Piperonyl Butoxide Residues from Plush Carpet in Experiment 6B by Drag Sled, PUF Roller, and Human Hand Press

	Deposition		Drag Sled		PUF Roller		Human Hand Press		
Block	Coupon Amount µg	Surface Loading ng/cm²	Transfer Amount µg	Transfer Rate ng/cm²	Transfer Amount µg	Transfer Rate ng/cm²	Subject Hand	Net Transfer Amount[a] µg	Transfer Rate ng/cm²
6-22-93 (Application)									
NE	1,029	4,980	126.6	167	51.0	67	AR	6.0	12
							BR	8.5	18
							CR	6.1	13
NW	1,200	5,810	135.6	178	56.8	75	AL	20.3	42
							BL	18.7	39
							CL	10.2	21
6-23-93									
CE	593	2,870	121.8	160	31.4	41	AL	12.3	26
							BL	5.9	12
							CL	4.8	10
CW	511	2,480	88.1	116	36.3	48	AR	9.1	19
							BR	8.2	17
							CR	6.5	14
6-24-93									
SE	850	4,120	81.5	107	46.6	61	AR	8.3	17
							BR	6.1	13
							CR	5.2	11
SW	826	4,000	29.6	39	40.6	53	AL	4.1	9
							BL	2.5	5
							CL	7.8	16
No. samples, n		6		6		6			18
Mean, x̄		4,040		127.9		57.6			17.4
Std. dev., s		1,250		52.1		12.5			9.7
Coef. of variation		0.31		0.41		0.22			0.56

a Net amount = crude handwipe amount - mean handwipe background = X - 0.1 µg

Table 51. Comparison of Transfers of Pyrethrin I Residues from Plush Carpet in Experiment 6B by Drag Sled, PUF Roller, and Human Hand Press

	Deposition		Drag Sled		PUF Roller		Human Hand Press		
Block	Coupon Amount µg	Surface Loading ng/cm²	Transfer Amount µg	Transfer Rate ng/cm²	Transfer Amount µg	Transfer Rate ng/cm²	Subject Hand	Net Transfer Amount[a] µg	Transfer Rate ng/cm²
6-22-93 (Application)									
NE	339	1,640	39.7	52.3	11.6	15.2	AR	INT[c]	
							BR	INT	
							CR	INT	
NW	415	2,010	42.2	55.5	16.1	21.2	AL	INT	
							BL	INT	
							CL	INT	
6-23-93									
CE	173	836	44.2	58.2	8.7	11.5	AL	<0.05	<0.10
							BL	<0.05	<0.10
							CL	<0.05	<0.10
CW	146	707	31.9	42.0	11.0	14.5	AR	<0.05	<0.10
							BR	<0.05	<0.10
							CR	<0.05	<0.10
6-24-93									
SE	175	846	5.2	6.8	14.0	18.4	AR	<0.05	<0.10
							BR	<0.05	<0.10
							CR	<0.05	<0.10
SW	183	886	9.1	12.0	11.5	15.1	AL	<0.05	<0.10
							BL	<0.05	<0.10
							CL	<0.05	<0.10
No. samples, n		6		6		6			12
Mean, x̄		1155		37.8		16.0			<0.10
Std. dev., s		536		22.7		3.4			
Coef. of variation		0.46		0.60		0.21			

a Since handwipe field blank amounts were <20 ng, no background is subtracted
b Excluded from summary statistics
c INT = Elevated background due to interference

Table 52. Comparison of Transfers of Chlorpyrifos Residues from Sheet Vinyl Flooring in Experiment 2 by Drag Sled, PUF Roller, and Human Hand Press

Block	Deposition		Drag Sled		PUF Roller		Human Hand Press		
	Coupon Amount µg	Surface Loading ng/cm²	Transfer Amount µg	Transfer Rate ng/cm²	Transfer Amount µg	Transfer Rate ng/cm²	Subject Hand	Net Transfer Amount[a] µg	Transfer Rate ng/cm²
8-10-93 (Application)									
NE	1,780	8,660	920	1,210	335	440	AR	85.6	178
							BR	89.4	186
							CR	157.1	327
NW	1,640	7,990	3,650	4,800	963	1,270	AL	348.0	726
							BL	333.0	695
							CL	93.6	195
8-11-93									
CE	2,000	9,770	1,010	1,330	560	740	AL	75.2	157
							BL	82.9	173
							CL	131.8	275
CW	2,700	13,170	1,040	1,360	293	390	AR	136.2	284
							BR	221.0	460
							CR	30.5	64
8-12-93									
SW	580	2,800	1,080	1,420	341	450	AL	69.0	144
							BL	59.5	124
							CL	45.0	94
SE	1,170	5,700	940	1,240	1,046	1,380	AR	186.0	388
							BR	34.9	72
							CR	19.1	40
No. samples, n		6		6		6			18
Mean, x̄		8,010		1,890		778			255
Std. dev., s		3,540		1,430		442			201
Coef. of variation		0.44		0.75		0.57			0.79

a Net amount = Crude handwipe amount - mean handwipe background = X - 0.3 µg

Table 53 Comparison of Transfers of Piperonyl Butoxide Residues from Sheet Vinyl Flooring in Experiment 7 by Drag Sled, PUF Roller, and Human Hand Press

	Deposition		Drag Sled		PUF Roller		Human Hand Press		
Block	Coupon Amount µg	Surface Loading ng/cm²	Transfer Amount µg	Transfer Rate ng/cm²	Transfer Amount µg	Transfer Rate ng/cm²	Subject Hand	Net Transfer Amount[a] µg	Transfer Rate ng/cm²
8-10-93 (Application)									
NE	1,670	8,130	730	960	240	320	AR	99	207
							BR	104	218
							CR	175	365
NW	1,310	6,380	2,760	3,640	624	820	AL	355	740
							BL	392	816
							CL	100	208
8-11-93									
CE	1,880	9,150	1,030	1,360	471	620	AL	100	208
							BL	106	220
							CL	160	333
CW	2,790	13,610	900	1,180	249	330	AR	161	335
							BR	242	504
							CR	38	78
8-12-93									
SW	720	3,530	1,170	1,540	279	370	AL	96	200
							BL	90	187
							CL	59	124
SE	960	4,680	970	1,270	990	1,300	AR	233	485
							BR	59	123
							CR	32	67
No. samples, n		6		6		6			18
Mean, x̄		7,580		1,660		626			301
Std. dev., s		3,620		990		387			213
Coef. of variation		0.48		0.60		0.62			0.71

a Since handwipe field blank amounts were <0.45 µg, no background is subtracted

Table 54. Comparison of Transfers of Pyrethrin I Residues from Sheet Vinyl Flooring in Experiment 7 by Drag Sled, PUF Roller, and Human Hand Press

	Deposition		Drag Sled		PUF Roller		Human Hand Press		
Block	Coupon Amount µg	Surface Loading ng/cm²	Transfer Amount µg	Transfer Rate ng/cm²	Transfer Amount µg	Transfer Rate ng/cm²	Subject Hand	Net Transfer Amount[a] µg	Transfer Rate ng/cm²
8-10-93 (Application)									
NE	284	1,380	101	133	68.5	90	AR	14.8	31
							BR	19.3	40
							CR	41.4	86
NW	288	1,390	168	221	113.0	149	AL	30.0	62
							BL	86.7	181
							CL	26.9	56
8-11-93									
CE	261	1,260	121	159	73.5	97	AL	10.9	23
							BL	9.1	19
							CL	7.1	15
CW	311	1,510	127	167	45.8	60	AR	18.4	38
							BR	26.2	55
							CR	1.6	3.0
8-12-93									
SW	122	590	201	265	48.1	63	AL	8.6	18
							BL	4.2	8.7
							CL	3.8	8.0
SE	229	1,110	160	210	182.0	240	AR	22.3	46
							BR	5.1	10
							CR	1.3	2.7
No. samples, n		6		6		6			18
Mean, x̄		1,210		192		116			39
Std. dev., s		330		49		68			42
Coef. of variation		0.27		0.25		0.59			1.08

a Since handwipe field blank amounts were <0.9 µg, no background is subtracted

Table 55 Comparison of Transfer of Fresh Dried Formulated Pesticide Residues from Flooring by Drag Sled, PUF Roller, and Human Hand Presses[a]

Experiment	Flooring	Applied Active Ingredient	Transfer Rate $(\bar{x} \pm s)$[b], ng cm^{2}, Using: Drag Sled (n=6)	PUF Roller (n=6)	Ten Hand Presses (n=18)
6A	Plush carpet (used)				
		Chlorpyrifos	5.6 ± 3.2	1.8 ± 1.0	d
		Piperonyl butoxide	7.0 ± 4.0	2.2 ± 1.1	d
		Pyrethrin I	1.0 ± 0.9	0.2 ± 0.1	d
6B	Plush carpet (used)				
		Chlorpyrifos[c]	9.2 ± 3.7	2.9 ± 0.3	1.3 ± 0.8
		Methoprene	2.5 ± 0.7	0.8 ± 0.5	0.3 ± 0.2
		Piperonyl butoxide	128 ± 52	58 ± 12	17. ± 10
		Pyrethrin I	38 ± 22	16 ± 3	
-	Sheet vinyl (new)				
		Chlorpyrifos	1890. ± 1430	780 ± 440	250. ± 200
		Piperonyl butoxide	1660 ± 990	630 ± 390	300 ± 210
		Pyrethrin I	192 ± 49	116 ± 68	39. ± 42

a Transfer by single pass over flooring using dry contact medium
b Mean and standard deviation of transfer rates from 0 to 2 days after application
c Transfer rates from 6 to 8 days after application
d Single hand press

Table 5c Percent Mean Transfer[a] of Fresh Chlorpyrifos Residues by Flooring and Transfer Method[b]

Experiment	Flooring	Mean Transfer, %[a]			
		Cloth Roller	Drag Sled	PUF Roller	Human Hand Press
1	Plush carpet (new)	4.9[c]	1.3	0.9[d]	
2	Level-loop carpet (new)	2.7[c]	1.7	1.5[d]	
3	Plush carpet (new)		0.41	0.26[d]	
5A	Plush carpet (used)			0.063	
5B	Plush carpet (used)			0.13	
5C	Plush carpet (used)			0.092	
5D	Plush carpet (used)		0.23		
5E	Plush carpet (used)		0.044		
6A	Plush carpet (used)		0.18	0.052	
7	Sheet vinyl (new)		36.1	10.3	4.6
8B	Plush carpet (used)		0.31	0.13	

a % mean transfer = 100 × (mean transfer rate, ng/cm²) / (mean surface loading, ng/cm²)
b Transfer of dry residue on day of application by single pass over flooring using dry contact medium
c 20 passes over flooring
d 2 passes over flooring

Table 57 Percent Mean Transfer[a] of Fresh Dried Residues by Flooring, Active Ingredient, and Transfer Method[b]

Experiment	Flooring	Application Method	Active Ingredient	Mean Transfer, %[a]: Drag Sled	Mean Transfer, %[a]: PUF Roller	Mean Transfer, %[a]: Human Hand Press
6A	Plush carpet (used)	Broadcast	Chlorpyrifos	0.10	0.03	
			Piperonyl butoxide	0.12	0.04	
			Pyrethrin I	0.19	0.04	
6B	Plush carpet (used)	Aerosol can	Methoprene	3.0	1.0	0.4
			Piperonyl butoxide	3.2	1.4	0.4
			Pyrethrin I	3.3	1.4	
7	Sheet vinyl (new)	Broadcast	Chlorpyrifos	24	9.7	3.2
			Piperonyl butoxide	22	8.3	4.0
			Pyrethrin I	16	9.6	3.2

a % mean transfer = 100 × (mean transfer rate, ng/cm^2)/(mean surface loading, ng/cm^2). Mean of transfer rates and surface loadings from 0 to 2 days after application.
b Transfer by single pass over flooring using dry contact medium.

Table 59 Stability of the Ratio of Transfers by Drag Sled and PUF Roller to Transfers by the Human Hand Press

			Mean Transfer Rate, ng cm^{-2}			Transfer Ratio[a]	
Exp	Date	Pesticide	Drag Sled (n=2)	PUF Roller (n=2)	Human Hand Press (n=6)	Drag Sled / Hand Press	PUF Roller / Hand Press
6B	6-22-93	Chlorpyrifos	9.0	2.9	0.81	11.0	3.6
		Methoprene	3.1	1.20	0.48	6.5	2.5
		Piperonyl butoxide	172	71	24.2	7.1	2.9
	6-23-93	Chlorpyrifos	12.1	3.0	2.06	5.9	1.5
		Methoprene	1.9	0.42	0.20	9.5	2.1
		Piperonyl butoxide	138	44	16.2	8.5	2.7
	6-24-93	Chlorpyrifos	6.5	3.5	0.99	6.6	3.5
		Piperonyl butoxide	73	57	11.8	6.2	4.9
[illegible]	8-10-93	Chlorpyrifos	3000	860	384	7.8	2.2
		Piperonyl butoxide	2300	570	426	5.4	1.3
		Pyrethrin I	177	119	76	2.3	1.6
	8-11-93	Chlorpyrifos	1350	560	236	5.7	2.4
		Piperonyl butoxide	1270	470	280	4.5	1.7
		Pyrethrin I	163	78	25.4	6.4	3.1
	8-12-93	Chlorpyrifos	1330	920	144	9.3	6.4
		Piperonyl butoxide	1400	840	198	7.1	4.2
		Pyrethrin I	238	152	15.7	15.1	9.6
No ratios, n						17	17
Mean, n						7.35	3.31
Std dev., s						2.84	2.10
Coef of variation						0.39	0.63

a Transfer ratio = Mean transfer rate by mechanical method (ng cm^{-2})/Mean transfer rate by human hand press (ng cm^{-2})

APPENDIX A

PROTOCOL FOR THE DETERMINATION OF WIPE REMOVAL EFFICIENCY OF CHLORPYRIFOS AND PYRETHRINS FORMULATED MIXTURE RESIDUES FROM HANDS (EXPERIMENT 4)

PROTOCOL FOR THE DETERMINATION OF WIPE REMOVAL EFFICIENCY OF CHLORPYRIFOS AND PYRETHRINS FORMULATED MIXTURE RESIDUES FROM HANDS (EXPERIMENT 4)

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Revised November 5, 1993 as Performed

TITLE: Protocol for the Determination of Wipe Removal Efficiency of Chlorpyrifos and Pyrethrins Residues from Hands (Experiment 4)

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PROJECT PERIOD: December 21, 1992 - January 29, 1993

I. INTRODUCTION AND OBJECTIVES

This is the fourth experiment of a study to compare sampling methods for the estimation of transfer of chemicals from contaminated surfaces (i.e. carpeting) to the skin. The methods are the Dow drag sled, the California cloth roller, and the Southwest Research Institute (SwRI) polyurethane foam (PUF) roller. These methods must be compared with each other, then with human skin pick-up before standardized methods can be established. Prior to the measurement of efficiency of the pick-up of chemicals by human skin, controlled experiments must be performed in order to determine the efficiency of removal of each chemical by the handwipe procedure and the efficiency of extraction of pesticides from the handwipe.

This experiment consists of three tasks. The experiment will be performed using pesticides at the lowest levels feasible to obtain meaningful analytical results. The specific tasks are:

A. Determine the elution efficiency of chlorpyrifos and pyrethrins formulated products from aluminum foil deposition squares.

B. Determine the extraction efficiency of chlorpyrifos and pyrethrins from isopropanol handwipes.

C. Determine the efficiency of removal of chlorpyrifos and pyrethrins from human hands by isopropanol wipes.

II. MATERIALS AND METHODS

A. Facilities Preparation.

All tasks will be conducted in the Elder trailer outside Building 70 on the grounds of Southwest Research Institute. A 2 ft x 6 ft piece of 1/4" thick plywood will be covered with solvent washed aluminum foil that has been taped in place.

6" x 6" Aluminum foil sampling squares will be cut from commercially available aluminum foil then solvent washed and dried prior to use.

Handwipes will be prepared from SOF-WICK 4" x 4" six ply dressing sponges. The sponges will be pre-extracted for 24 hours with hexane then for an additional 24 hours with acetone. Sets of two sponges will then be packaged in aluminum foil to prevent contamination prior to use.

The pesticide formulated mixture will be prepared by adding sufficient Pyrethrins to Raid Formula 1 (0.25 % chlorpyrifos and 0.08 % pyrethrins) to increase the pyrethrins levels to 5 %. A diluted formulated mixture solution (1:25 dilution) will then be prepared that contains 100 ng/µL chlorpyrifos and 2000 ng/µL pyrethrins.

B. Application of pesticides to Aluminum Foil Deposition Squares.

A volume of 50 µL of the diluted pesticide formulated mixture will be applied to each 6" x 6" aluminum foil square. Aluminum foil squares that will be used for the hand-press procedure will be taped to the aluminum foil backing. The mixture will be applied in a fashion so that the pesticides are concentrated in approximately a 2" diameter area in the center of the foil. Prior to hand application or extraction the aqueous solvent will be allowed to evaporate.

C. Hand-press Method.

Since the purpose of this study is to investigate the wipe removal efficiency of the handwipe and not the uptake of pesticides onto the hand, a precise and reproducible procedure for the hand press is not necessary. However, a method is needed that will efficiently transfer most of the pesticide from the foil to the hand. Prior to each hand press, each subject will be requested to thoroughly wash his or her hands with soap and water. The subject will be cautioned to avoid touching any surfaces prior to the handwipe procedure. Each subject will then place a powder-free vinyl glove over one hand to prevent contamination while performing the wipe procedure on the first hand and to prevent the isopropanol from drying out the skin prior to the handwipe resulting in an abnormal skin condition that could affect wipe removal efficiency. Each subject will then be asked to initially to press and rotate the palm of the hand to the 2" dia. area of pesticides with fingers held off of the surface. The subject will then be asked to press and rotate the front and back of the fingers on the foil.

D. Isopropanol Handwipe Method

Following deposition of the target pesticides onto the hand, an isopropanol handwipe of the hand will be performed. The handwipe procedure will be that described by Camann et al. (1992). The handwipe will consist of two SOF-WICK 4" x 4" 6-ply dressing sponges which have been pre-cleaned prior to use. Each sponge will be laced with 10 mL of OPTIMA grade isopropanol. The subject will be asked to perform a general wipe of each hand with the first sponge. The second sponge will be used to wipe around and between each digit. Both sponges will then be placed in a single container and an additional 50 mL of isopropanol will be added. The subject will perform all actual handling of the sponges from preparation to placement in the sample container. Immediately following each handwipe procedure, the subject will thoroughly wash his hands to remove any remaining pesticides residues.

E. Extraction of Pesticides from Aluminum Foil Deposition Squares

Following the deposition of the pesticide formulated mixture (in the case of control samples) or following the hand-press procedure, the 6" x 6" aluminum foil squares will be placed in solvent washed and oven dried 1 lb wide-mouth jars fitted with teflon lined lids. Any tape used to hold the squares to the board will be removed prior to extraction. A 300 mL volume of 1:1 ether:hexane will be added to each jar. Terphenyl-d_{14} will be added as a surrogate in sufficient quantity to result in a concentration of 1.0 ng/µL in the final extract. The jars will then be shaken for 30 min. The ether-hexane extract will then be concentrated to a volume of 1.0 mL in hexane for GC/MS analysis.

F. Extraction of Pesticides from Isopropanol Handwipes

Following the hand-press and handwipe procedures, the handwipes will be extracted for the target pesticides using the method described by Camann et al. (1992). Immediately prior to extraction, terphenyl-d_{14} surrogate will be added and the jars will be shaken for five minutes. The isopropanol will then be drained from the jar into a 250 mL flat bottom flask. The handwipes will be extracted twice with two 50 mL portions of 1:1 diethyl ether:hexane by shaking for one minute. The gauze pad will then be squeezed to remove solvent and the jar will be rinsed three times with hexane. All rinsates and extracts will then be combined in the 250 mL round bottom flask. The ether/hexane/isopropanol extracts will then be concentrated to a volume of 1.0 mL in hexane for GC/MS analysis.

G. Analysis of Pesticides Extracts

Each handwipe and aluminum foil extract will be analyzed for chlorpyrifos and pyrethrins on a Fisons MD800 gas chromatograph/mass spectrometer (GC/MS) operating in a selected ion recording mode. A primary quantitation ion and secondary confirmation ion will be selected for chlorpyrifos and each of the six pyrethrins. The GC/MS will be calibrated from 0.05 to 1.0 ng/µL for chlorpyrifos and 1.0 ng/µL to 20 ng/µL for total pyrethrins. This corresponds to a quantitation limit of 50 ng per handwipe for chlorpyrifos and 1 µg per handwipe for pyrethrins. Sample extracts containing target analytes at levels beyond the calibration range will be diluted and reanalyzed.

III. EXPERIMENTAL DESIGN

A. Task 4A. Determination of Aluminum Foil Elution Efficiency

In order to determine the efficiency of removal of the target pesticides from aluminum foil squares, seven foils will be spiked with 250 µL of the diluted formulated mixture. An additional seven foils will be spiked with 25 µL of the formulated mixture. The factor of ten difference in spike levels will determine if aluminum foil elution efficiency is independent of the amount of pesticide spiked. Two additional foils will be extracted without spiking to serve as control blanks. In order to verify the level of the pesticides in the spike solution, two 300 mL portions of 1:1 ether:hexane will be spiked with 250 µL of the diluted formulated mixture and two additional portions of ether:hexane will be spiked with 25 µL of the diluted formulated mixture. All foils, control blanks and solvent spikes will be extracted and analyzed as described above.

B. Task 4B. Determination of Handwipe Extraction Efficiency

Efficiency of the extraction method for removal of the target pesticides from the handwipes will be evaluated by spiking seven moistened, precleaned handwipes with 250 µL of the diluted formulated mixture. An additional seven wipes will be spiked with 25 µL of the diluted formulated mixture. The factor of ten difference in spike levels will determine if the handwipe extraction efficiency is independent of the amount of pesticide spiked. Two handwipes will be extracted without spiking and will serve as control blanks, two aliquots of isopropanol will be spiked with 250 µL of the diluted formulated mixture and two aliquots will be spiked with 25 µL of the diluted formulated mixture. All handwipes and spikes will be extracted and analyzed as described above.

C. Task 4C. Determination of Handwipe Removal Efficiency

Handwipe removal efficiency experiments will be performed using two human subjects volunteers over a three day period. Mr. David E. Camann and Dr. Paul W. Geno of the Department of Environmental Chemistry at SwRI will serve as the subjects. On each day prior to sampling, the subject's hands will be inspected by Dr. Nicholas Giardino for rashes, abrasions or cuts in the skin.

When any such sores exist, the experiment will be postponed until the hand heals. On Days 1 and 2, five aluminum foil squares will be spiked with 50 µL of the diluted formulated mixture as described above, one aluminum foil square will be spiked with 25 µL of the diluted formulated product and one foil square will serve as a control blank. Hand presses will be performed on four of the 50 µL spiked aluminum squares, corresponding to each hand of each of the two subjects. The order in which the two hands are sampled will alternate on the two days. On Day 3, three aluminum foil squares will be spiked with 50 µL of the diluted formulated mixture and one aluminum foil square will be spiked with 25 µL of diluted formulated mixture. Hand presses will be performed on two of the 50 µL spiked squares. Isopropanol handwipes will be immediate performed following the hand presses. On each day, one additional handwipe will be spiked directly with 50 µL of the diluted formulated mixture, one handwipe will be spiked with 25 µL of the diluted formulated mixture and one handwipe will serve as a control blank. In order to verify the level of the pesticides in the spike solution, one 300 mL portion of 1:1 ether:hexane will be spiked with 50 µL of the diluted formulated mixture, one additional portion of ether:hexane will be spiked with 25 µL of the diluted formulated mixture and one portion will serve as an extraction blank. All handwipes and foils will be extracted as described above immediately following the handwipe procedure. A summary of samples for the three described tasks is given in Table 1.

IV. CALCULATIONS

Following completion of Task 4A, the elution efficiency (E_{el}) of the aluminum foil extraction procedure for each pesticide will be calculated by:

$$E_{el} = M_{fex}/M_{app}$$

where M_{fex} is the amount of each pesticide determined to be extracted from each foil by analysis and M_{app} is the amount of each pesticide applied from the foil. The mean ($\bar{E}_{el}$) and coefficient of variation of the elution efficiency will then be calculated over the ten replicates at each level.

Following the completion of Task 4B, the extraction efficiency of the handwipe extraction method (E_{ex}) will be calculated by

$$E_{ex} = M_{wipe}/M_{sp}$$

where M_{wipe} is the amount of each pesticide determined to be extracted from each handwipe by analysis and M_{sp} is the amount of each pesticide applied to the handwipe. The mean ($\bar{E}_{ex}$) and coefficient of variation of the extraction efficiency will then be calculated over the ten replicates at each level.

The wipe removal efficiency (RE) can then be calculated for each replicate handwipe of Task 4C using the following equation:

$$RE = (M_{wipe}/\bar{E}_{ex})/[M_{app} - (M_{fex}/\bar{E}_{el})]$$

where M_{wipe} is the analytically determined amount of each pesticide wiped from the hand, $\bar{E}_{ex}$ is the mean extraction efficiency of the handwipe extraction method determined in Task 4B for the low level spike, M_{app} is the known amount of each pesticide applied to the foil prior to hand press, M_{fex} is the analytically determined amount of each pesticide remaining on the foil following hand press and $\bar{E}_e$ is the mean elution efficiency of the aluminum foil extraction determined in Task 4A for the low level spike. The mean removal efficiency and coefficient of variation for each subject, and the mean removal efficiency and coefficient of variation for all samples will be calculated.

V. ESTIMATION OF HUMAN EXPOSURE

The maximum exposure to subjects is 5 μg/hand of chlorpyrifos and 100 μg/hand for pyrethrins. This estimate assumes 100% of the pesticides applied to the foil are picked-up by the hand and absorbed through the skin. According to our modeled results for flux through the dermal layer of the hand, we determined for each hand press that 0.09 ng of pyrethrins and 1 μg of chlorpyrifos will be absorbed (Droz, et. al (1991) and Fiserova-Beberova, et. al (1989)). It is assumed the total surface area of the hand is 900 cm^2 (within the range of surface areas provided by the EPA Interim Report on Dermal Exposure, January 1992), and that the exposure time is 5 minutes. The model assumes that a completely saturated water solution of the chemical is applied to the skin of the hand.

In these experiments the dried pesticide residue will be wiped from the hands using isopropanol. This solvent is likely to enhance the absorption of the pesticides into the skin.

One must be cautious whenever using and interpreting modeled results. However, this model has been used and extensively tested by others (see above references) and was a good predictor for dermal absorption of chemicals with molecular weights below 500. According to the modeled results the absorbed amount of pyrethrins for the entire experiment is negligible. The predicted absorption of chlorpyrifos is higher, but is still low.

The rabbit LD_{50} dermal for chlorpyrifos is 2000 mg/kg and rat dermal LD_{50} for pyrethrins greater than 1800 mg/kg (Farm Chemicals Handbook '92). There is very little chance for severe adverse health effects to occur.

For short-term exposures, pyrethrins are contact allergenic compounds, can cause dermatitis, and may mildly irritate the eyes, nose, and throat. Long-term exposure can lead to organ toxicity, excluding the nervous, respiratory, hematological, or reproductive systems. Chlorpyrifos can cause nervous system disturbances, and represents an acute and chronic hazard. These health advisories were taken from Patty's Industrial Hygiene And Toxicology, Volume IIIA (1985) and concern workplace exposures. It is expected that these workplace exposures are substantially higher than those predicted during this set of experiments.

The acute exposures predicted to be received during this experiment for chlorpyrifos are 1 μg/hand for a total of 2 μg, and for pyrethrins 0.09 ng/hand for a total of 0.18 ng. Since all the recognized industrial hygiene organizations (ACGIH, OSHA, NIOSH, MAK) have a skin notation for chlorpyrifos, those participating in the experiment will wash their hands immediately after exposure to either of the pesticides. The skin notation for healthy workers addresses adverse health effects occurring if a worker comes into contact with the pure chemical. Industrial and agricultural exposures (Camann et al. (1992)) would be several orders of magnitude above what the participants in this experiment will receive.

Lastly, those with any abnormal skin condition such as eczema, a rash, abrasions, cuts, or any breaks in the skin will not be eligible to participate in the experiment.

VI. REFERENCES

Camann, D.E., Geno, P.W., Harding, H.J., Clothier, J.M., and Giardino, N.J. (1992). Evaluation of Environmental Exposure Assessment Methods for the NCI/EPA Farm Occupation Exposure Study (NEOFOS). EPA Contract Number 68D10150, Southwest Research Institute Project 01-5278-100, San Antonio, TX.

Droz, P.O., Berode, M., and Wu, M.M. (1991). Appl. Occup. Environ. Hyg., 465-474.

Fiserova- Berberova, V., and Pierce, J.T. (1989). Appl. Indus. Hyg. 8: F-14 - F-21.

Table 1. Experimental Design for the handwipe removal efficiency study.

Task 4A.	250 µL Formulated Mixture (H)	25 µL Formulated Mixture (L)	Blank (B)	Total Analyses
Al Foil Sq. (FS)	7	7	2	16
Extraction Solvent Spikes (SS)	2	2	2	6

Task 4B.	250 µL Formulated Mixture (H)	25 µL Formulated Mixture (L)	Blank (B)	Total Analyses
Isopropanol Handwipes (HW)	7	7	2	16
Extraction Solvent Spikes (SS)	2	2	2	6

Task 4C Day 1.	50 µL Formulated Mixture (H)	25 µL Formulated Mixture (L)	Blank (B)	Total Analyses
Al Foil Sq. (FS)	5	1	1	7
Hand presses				
Subj. A (HA L/R)	2			
Subj. B (HB L/R)	2			
Isopropanol Handwipes (HW)	4+1	1	1	7
Extraction Solvent Spikes (SS)	1	1	1	3
Task 4C Day 2.				
Al Foil Sq. (FS)	5	1	1	7
Hand presses				
Subj. A (HA L/R)	2			
Subj. B (HB L/R)	2			
Isopropanol Handwipes (HW)	4+1	1	1	7
Extraction Solvent Spikes (SS)	1	1	1	3

Table 1. Cont.

Task 4C Day 3

Al Foil Sq. (FS)	3	1	1	5
Hand presses				
Subj. A (HA L/R)	1			
Subj. B (HB L/R)	1			
Isopropanol Handwipes (HW)	2+1	1	1	5
Extraction Solvent Spikes (SS)	1	1	1	3
Total Analyses				91

Sample I.D. will be the task number followed by the medium followed by the spike level followed by the replicate (or the day for Task 4C), e.g. the foil square for the right hand replicate of Subject B hand press on Day 2 would be labeled 4C-FS-HBR-H-2.

APPENDIX B

PROTOCOL FOR THE COMPARISON OF TRANSFERS BY THE DRAG SLED, PUF ROLLER, AND HUMAN HAND PRESS OF CHLORPYRIFOS AND PIPERONYL BUTOXIDE FORMULATED MIXTURE RESIDUES FROM SHEET VINYL FLOORING (EXPERIMENT 7)

PROTOCOL FOR THE COMPARISON OF TRANSFERS BY THE DRAG SLED, PUF ROLLER, AND HUMAN HAND PRESS OF CHLORPYRIFOS AND PIPERONYL BUTOXIDE FORMULATED MIXTURE RESIDUES FROM SHEET VINYL FLOORING (EXPERIMENT 7)

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JULY 30, 1993

TITLE: Protocol for the Comparison of Transfers by the Drag Sled, PUF Roller, and Human Hand Press of Chlorpyrifos and Piperonyl Butoxide Formulated Mixture Residues from Sheet Vinyl Flooring (Experiment 7)

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EPA Contract 68-DO-0007

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PROJECT PERIOD: August 4, 1993 - September 15, 1993

I. INTRODUCTION

Dermal contact with residues of pesticides applied to carpets and subsequent skin absorption or ingestion through hand-to-mouth activity are routes of human exposure which need better evaluation, especially for young children. The Dow drag sled, the California cloth roller, and the Southwest Research Institute (SwRI) polyurethane foam (PUF) roller (SwRI invention disclosure #2061, patent pending) are dislodgeable residue sampling methods which have recently been developed to estimate the transfer of a chemical from a contaminated surface to the skin. These methods need to be compared to determine which provides the most accurate, reproducible, economical, and facile performance. Precision and bias relative to human skin pick-up must also be determined before standardized methods can be established for use by registrants and researchers.

After chlorpyrifos which was broadcast-sprayed on carpet had dried, transfers by the drag sled, the cloth roller, and the PUF roller were compared in Experiments 1 to 3 (Camann et al., 1993). On plush nylon carpet, mean chlorpyrifos transfers were 4.5% by the cloth roller, 1.1% by the drag sled, and 0.65% by the PUF roller (Experiment 1). On level-loop polypropylene carpet, mean transfers were 2.5% by the cloth roller, 1.4% by the drag sled, and 1.2% by the PUF roller (Experiment 2). The cloth roller was found to be less suitable than the other methods because its transfers exhibited greater variability and were altered by orientation of the roll relative to the lay of the carpet fibers. Moistening the sampling media increased the transfer by the drag sled and the PUF roller, but substantially increased the measurement variability of both methods (Experiment 3).

Experiment 4 determined the removal efficiency of two pesticides (chlorpyrifos and pyrethrins) that had been applied to human skin. Experiment 5 evaluated the effects of sampling pressure, traverse distance, number of repeat passes over the same section of carpet, speed, and air temperature on dislodgeable residue transfer of chlorpyrifos by the PUF roller and drag sled. Preliminary results indicate that air or carpet temperature had a marked effect on transfer, especially by the drag sled, but this effect was deduced from a series of tests performed on different days. Experiments are being conducted to compare human hand presses and mechanical dislodgeability of several pesticide residues (chlorpyrifos, pyrethrins and piperonyl butoxide) from plush carpet (Experiment 6), and to determine the direct effect of the temperature of the air and carpet on transfer of chlorpyrifos, pyrethrins, and piperonyl butoxide residues from plush carpet using both the drag sled and the PUF roller in tests performed on the same day (Experiment 8).

This protocol describes Experiment 7, in which comparisons will be made between hand presses and both the drag sled and the PUF roller in the transfer of chlorpyrifos and piperonyl butoxide residues from new sheet vinyl flooring.

II. MATERIALS AND METHODS

A. Facility Preparation

An empty room (9' x 15') in a 42' x 10'3-room trailer on the SwRI Campus will be used to do the experiment. The plush cut-pile nylon carpet and pad will be removed and Armstrong Explorer Solarian sheet vinyl installed on a wood underlayment over the old floor. The sheet vinyl will be rinsed with clean water.

B. Dislodgeable Residue Methods

Relevant characteristics of the dislodgeable residue methods (i.e., the Dow drag sled and the SwRI PUF roller) and the human hand press are summarized and contrasted in Table 1.

TABLE 1. CHARACTERISTICS OF DISLODGEABLE RESIDUE AND HAND PRESS METHODS

	DOW DRAG SLED	SWRI PUF ROLLER (October 1992 Model)	HUMAN HAND PRESS
Sampling Medium	Denim weave cloth (predominantly cotton)	Polyurethane foam (PUF) ring (0.029 g/cm^3, polyether)	Skin on palm of hand
Surface of Sampling Medium	Square (10.2 cm)^2	Curved exterior of ring(OD = 8.9 cm, length = 7.6 cm)	Palm (ca. 8 cm x 8 cm)
Contact Motion	Drag	Roll	Ten Presses (for 1s)
Face (Instantaneous Pressed Contact Area through Sampling Medium)	7.6 cm x 7.6 cm = 58 cm^2	7.6 cm x 5.1 cm = 38.6 cm^2	7.6 cm x 7.6 cm = 58 cm^2
Mass Exerting Pressure Through Sampling Medium	3.46 kg	3.10 kg	NA
Pressure Exerted Through Sampling Medium	5,900 Pa = (3.46 kg)(9.8 m/s^2)/(0.076 m)^2	8,000 Pa = (3.10 kg)(9.8 m/s^2)/[(0.076 m)(0.05 m)]	6,900 Pa = 1.0 psi
Sampled Carpet Area	7.6 cm x 1.0 m = 0.076 m^2	7.6 cm x 1.0m = 0.076 m^2	10 x 7.6 cm x 6.3 cm = 0.048 m^2
Number of Passes over Sampled Carpet Area	1	1	1
Sampling Speed over Carpet	0.07 m/s	0.10 m/s	NA

The drag sled method will be performed using the initial configuration described by Vaccaro and Cranston (1990). Briefly, a precleaned dry 4" x 4" denim weave cloth supplied by B. Shurdut, Dow Chemical Company, is attached beneath foil under a 3" x 3" plywood block on which an 8-lb. weight is mounted (Figure 1). From a stationary position on aluminum foil, the sled is dragged once over a 3" x 1 m carpet strip at 6-8 cm/s. After the single pass, the denim cloth is removed for analysis. Except for the weighted plywood block (current model unavailable since in use at Dow), Dow still performs its drag sled method as initially described (personal communication, B. Shurdut, July 1992).

The new (October 1992) model of the PUF roller sampler (Camann et al., 1993b) will be used instead of the original PUF roller sampler (Hsu, et al., 1990). A precleaned dry PUF ring (3" length, 3.5" OD, 1.62" ID) is secured on the 3" length x 1.75" OD cylindrical 0.37 kg aluminum roller (Figure 2). From a stationary position on aluminum foil, the PUF roller is rolled once over a 3" x 1.0 m carpet strip at 10 cm/s. After the pass, the PUF ring is removed from the roller for analysis.

C. Hand Press and Wipe Methods

A set of ten presses of the treated vinyl will be made with each hand by three subjects on three days in a reproducible manner. Prior to each daily pair of hand presses, each subject will be requested to thoroughly wash his hands with soap and water. The subject will be cautioned to avoid touching any surfaces during the hand press and wipe sequence. The subject will then place a disposable nitrile glove over the non-test hand. The second hand is gloved to prevent contamination while performing the press and wipe procedure on the first hand and to prevent the isopropanol from drying out the skin of the second hand prior to the hand press (avoiding an abnormal skin condition that could affect hand press transfer efficiency). A card-stock template will be placed over the designated area for vinyl sampling to expose a 3 in (7.6 cm) x 25 in (63.5 cm) vinyl strip. While kneeling on a cardboard mat, each subject will perform a series of ten presses of the palm of the test hand to adjacent sections of vinyl exposed by the template at a pressure of ca. 1.0 psi for 1 sec each with fingers held off of the surface. An isopropanol handwipe of the hand will be performed as described by Camann et al. (1992) in a clean area away from the trailer. After washing both hands with soap and water, the glove will be removed from the second test hand and a clean glove placed over the second non-test hand. The press and wipe procedures described above will then be repeated using the second hand.

The handwipe will utilize two SOF-WICK® 4" x 4" 6-ply dressing sponges which have been pre-cleaned prior to use. Each sponge will be laced with 10 mL of OPTIMA grade isopropanol. The subject will be asked to perform a general wipe of each hand with the first sponge. The second sponge will be used to wipe around and between each digit. Both sponges will then be placed in a single container and an additional 50 mL of isopropanol will be added. The subject will perform all direct handling of the sponges from preparation to placement in the sample container, although handling via forceps is also permitted. Immediately following each handwipe procedure, the subject will thoroughly wash his hands to remove any remaining pesticides residues.

D. Broadcast Application of Chlorpyrifos/Pyrethrins/Piperonyl Butoxide Formulated Mixture and Ventilation While Drying

Broadcast application of a chlorpyrifos/pyrethrins/piperonyl butoxide formulated mixture to test vinyl flooring will be conducted by a licensed pest control applicator according to label instructions to control a light infestation of fleas. The formulated emulsifiable concentrate products, Dursban® L.O. (E.P.A. Registration No. 62719-55), which contains 41.5% chlorpyrifos (O,O-diethyl O-[3,5,6-trichloro-2-pyridyl]phosphorothioate), and Kicker® (EPA Registration No. 4816-707AA), which contains 6.0% pyrethrins and 60.0% technical piperonyl butoxide will be tank mixed at 2/3 fl. oz. (20 mL) Dursban® L.O. and 0.5 fl. oz. (15 mL) Kicker® per gallon of water to yield 0.25 % chlorpyrifos, 0.025% pyrethrins, and 0.25% piperonyl butoxide in the aqueous spray. The mixture will be applied approximately 40 cm above the vinyl at a rate of 1 gallon of diluted mixture per 1600 square feet with a hand-held fan broadcast nozzle attached to an air pressurized tank. Application will be accomplished in ca. 2 min.

The trailer will be ventilated for 2 h immediately after application. All windows will be opened and window air conditioning units operated in fresh return air mode. During the first 30 min and last 15 min of the ventilation period, both doors will be opened and a box fan operated outside the test room doorway to allow maximum cross ventilation. Air conditioner units will be returned to the usual recirculated air mode just prior to sampling and remain on throughout the sampling period.

E. Experimental Design

Adjacent samples using both dislodgeable residue methods, a hand press by each subject, and two deposition coupons will be collected sequentially within a rectangular block of treated vinyl. Six replicate blocks will be sampled over three days so that each hand is pressed and wiped only once per day (to limit dermal exposure and to allow return of normal levels of natural oils to the skin before each hand press). The experimental design is presented in Table 2 and the physical layout for sampling is shown in Figure 1. Sampling will be performed at approxiomately the same floor temperature (~25 °C) and room air temperature each day.

Deposition coupons, consisting of Teflon squares (4 in. x 4 in.) will be placed on the vinyl prior to the pesticide application and picked up before the adjacent dislodgeable residue samples from the block are collected. Residues measured on the coupon pair give an estimate of the surface loading of residue remaining on adjacent vinyl flooring during sampling in the block.

Field blank wipes of both hands of each subject will be made in the clean area after a set of ten presses with the hand on the untreated vinyl on Days 1 and 2. Two field blanks of both mechanical methods will be obtained by sampling on the vinyl on the day prior to the pesticide application (Day 2). The field blanks will assess residues transferred via air and contamination potential during sampling and handling. Deposition coupons will be placed at two designated locations in each sampling block shortly before the application commences on Day 3. Field samples will be collected in two blocks each on the afternoons of Days 3, 4, and 5 after label allowed re-entry on Day 3 (i.e., when the vinyl is dry). The dislodgeable residue and hand press samples of a block will be collected from specified locations in the block after the deposition coupons are picked up (see Figure 1). All samples will be collected in one block before proceeding to the next block. Spikes of the precleaned dislodgeable residue and wipe matrices and of a deposition coupon pair will be made both before (Day 3) and after (Day 5) the replicate block sample sets are collected; these field spikes will be used to assess and adjust for losses during transport, storage, and extraction.

F. Sample Analysis

Dislodgeable residue samples will be Soxhlet-extracted with 6% ethyl ether/94% hexane; extraction will commence within 24 hours after sampling. The pair of deposition coupons from a block will together be rinsed with 6% ether-hexane as a single sample. Isopropanol-saturated handwipes will be shake extracted with 1:1 diethyl ether:hexane (Camann et al., 1992). Extracts will be analyzed for chlorpyrifos, pyrethrins and piperonyl butoxide on a Fisons MD 800 GC/MS operating in selected ion monitoring mode.

G. Data Adjustment

Crude wipe results will be adjusted for wipe removal efficiency from the hand by dividing by the mean removal efficiency determined in Experiment 4. It is anticipated that hand wipe results for pyrethrins may be less than the detection limit. The wipe removal efficiency for piperonyl butoxide will be assumed to be between the mean removal efficiecies determined for chlorpyrifos and pyrethrins.

Crude results (mg/sample) from each field sample will be adjusted for contamination and extraction inefficiency by subtracting the field blank mean and dividing the difference by the mean recovery proportion of the field spikes for that method. The adjusted result will be divided by the vinyl area (see Table 1) to determine the measured transfer rate (mg/m^2 of vinyl contacted) for dislodgeable residue and hand wipe samples and the measured surface loading (mg/m^2) for coupon samples.

III. ESTIMATION OF HUMAN EXPOSURE

A. Selection and Recruitment of Subjects

Three normal male subjects, 35 to 49 years of age, have volunteered to perform the hand presses of treated vinyl as described herein. They are Mr. David E. Camann, principal investigator, Dr. Paul W. Geno, investigator, and Dr. Jong-Pyng Hsu, Director, Department of Environmental Chemistry. Informed consent will be obtained from each subject by Mr. Camann before the experiment commences; the consent forms will be kept in Mr. Camann's office in Bldg. 70, Office 17.

Those subjects with any abnormal skin condition such as eczema, a rash, abrasions, cuts, or any breaks in the skin will not be eligible to participate in the experiment, until the condition heals.

B. Estimated Exposure of Subjects

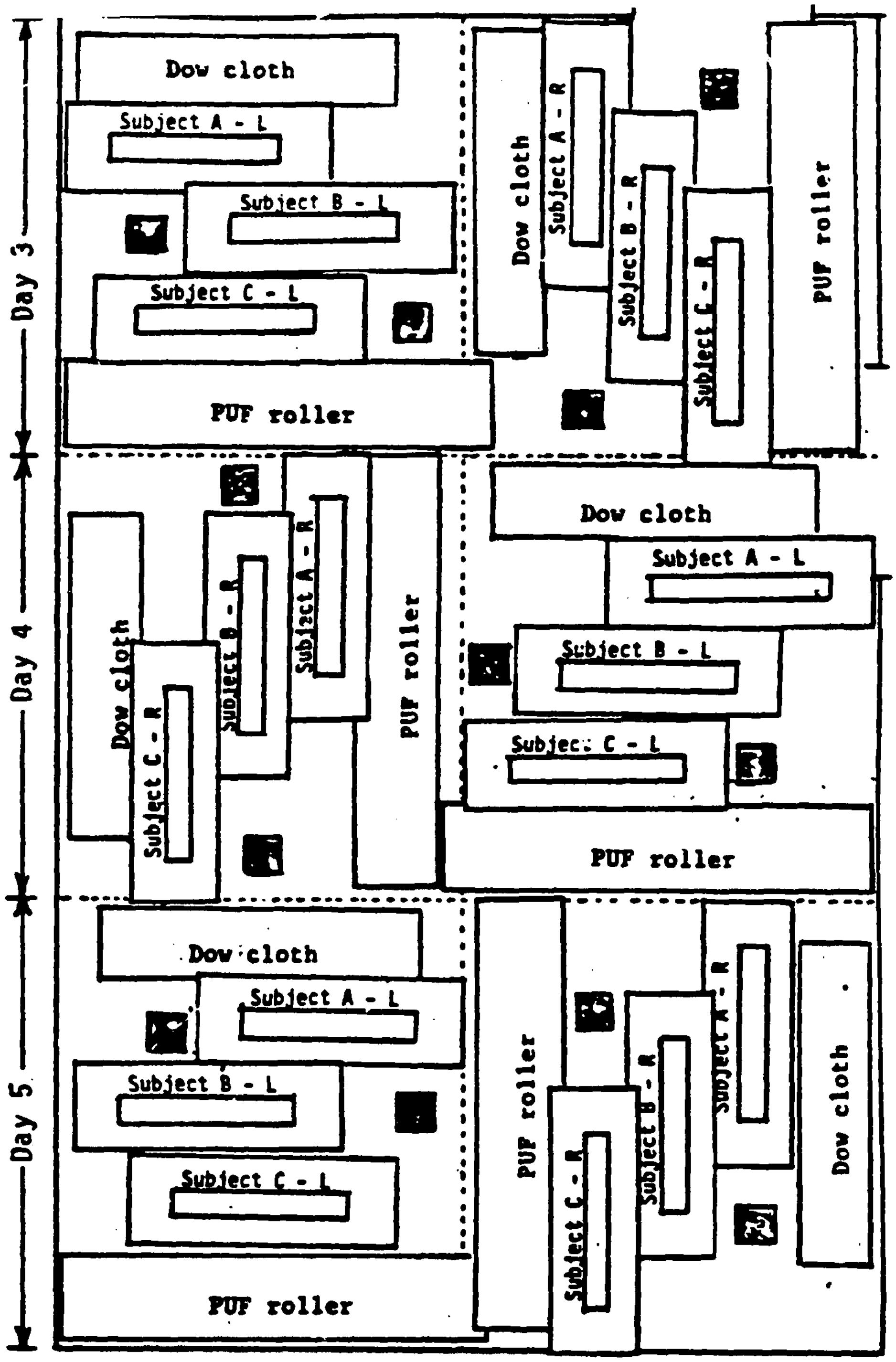
In Experiment 1, broadcast application of a 0.5% aqueous spray of chlorpyrifos at 1 gal/ 1600 ft^2 during summer produced a loading of 154 mg/m^2 on the plush cut-pile nylon carpet (Camann et al., 1993b). Thus, an aqueous spray of 0.25% chlorpyrifos, 0.025% pyrethrins, and 0.25% piperonyl butoxide in Experiment 7 applied by the same application method at the same rate in the same season should produce loadings of approximately 77 mg chlorpyrifos/m^2, 7.7 mg pyrethrins/m^2, and 77 mg piperonyl butoxide/m^2 during sampling on the application day, Day 3. Fenske et al (1991) found that

TABLE 2. EXPERIMENT 7: COMPARISON OF CHLORPYRIFOS AND PIPERONYL BUTOXIDE RESIDUE TRANSFERS FROM SHEET VINYL FLOORING BY DRAG SLED SAMPLER, PUF ROLLER SAMPLER, AND HAND PRESS BY THREE HUMAN SUBJECTS

		Sample Analyses									
					Hand Press						
					Subject A		Subject B		Subject C		
Day	Sample Category	Deposition Coupon	Drag Sled	PUF Roller	L	R	L	R	L	R	Total
1	Field Blanks	0	0	0	1	1	1	1	1	1	6
2	Field Blanks	0	2	2	1	1	1	1	1	1	10
3-AM	Pesticide application										
3-AM	Field Matrix Spikes	1[a]	1	1	1		1				5
3-PM	DR Samples[b]	2[a]	2	2	1	1	1	1	1	1	12
4-PM	DR Samples[b]	2[a]	2	2	1	1	1	1	1	1	12
5-PM	DR Samples[b]	2[a]	2	2	1	1	1	1	1	1	12
5-PM	Field Matrix Spike	1[a]	1	1		1		1			5
Total DR Samples		6	6	6	6		6		6		36
Total Field Blanks		0	2	2	4		4		4		16
Total Field Matrix Spikes		2	2	2	2		2		0		10
Total Samples		8	10	10	12		12		10		62

a The two Teflon coupons in a block are combined and extracted together as a single sample.

b The samples collected from different treated vinyl areas within each block are two deposition coupons, one drag sled, on PUF roller, and one press/wipe by each subject of the same hand.



Sample Layout for Experiment 7: Hand Press Collection Efficiency on Vinyl Sheet Flooring

- **Day 3 - North block**
  - **4 deposition coupons**
  - **2 PUF roller samples (with, across)**
  - **2 Dow cloth samples (with, across)**
  - **6 hand presses (both hands of subjects A, B, & C)**
- **Day 4 - Center block**
  - **4 deposition coupons**
  - **2 PUF roller samples (with, across)**
  - **2 Dow cloth samples (with, across)**
  - **6 hand presses (both hands of subjects A, B, & C)**
- **Day 5 - South block**
  - **4 deposition coupons**
  - **2 PUF roller samples (with, across)**
  - **2 Dow cloth samples (with, across)**
  - **6 hand presses (both hands of subjects A, B, & C)**

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Figure 1. Sampling Layout for Experiment 7.

mean chlorpyrifos wipe residues from treated carpet after 24 hr were only 30-40% of the wipe residues 1-7 hr post-application. In two recent experiments, the mean amount of chlorpyrifos transferred from a plush nylon carpet three days after application was 15% and 25% of the amount transferred by the PUF roller after drying on the application day. Hence the loadings for Days 4 and 5 of Experiment 7 can be anticipated to be about 35% and 27% of the Day 3 loadings, respectively:

Chlorpyrifos:	27 mg/m² on Day 4; 21 mg/m² on Day 5
Pyrethrins:	2.7 mg/m² on Day 4; 2.1 mg/m² on Day 5
Piperonyl butoxide:	27 mg/m² on Day 4; 21 mg/m² on Day 5

The percentages of analytical standard residues of 13 pesticides (including chlorpyrifos) on aluminum foil which were transferred to skin by a series of ten sequential 1s hand heel presses by two of the study subjects were nearly equivalent to the mean percentage transfers by the PUF roller (e.g., 7.7% by Subject 1 and 8.9% by Subject 2 vs. 7.1% mean by PUF roller for chlorpyrifos) (Hsu et al., 1990). Thus, hand press transfers from sheet vinyl in Experiment 7 can be expected to be similar to, or less than, the mean 8.3% transfer of chlorpyrifos from aluminum foil by the two subjects. To be conservative, a transfer of 10% will be assumed. Using an exposed palm area of the hand of 0.0058 m², the residue on both palms of each subject after the hand presses on Day 3 can be estimated as:

Chlorpyrifos:	(77 mg/m²) x (0.10 transfer/press) x (10 presses) x (0.0058 m²/press) x (2 palms) = 890 µg
Pyrethrins:	(7.7 mg/m²) x (0.10 transfer/press) x (10 presses) x (0.0058 m²/press) x (2 palms) = 89 µg
Piperonyl butoxide:	(77 mg/m²) x (0.10 transfer/press) x (10 presses) x (0.0058 m²/press) x (2 palms) = 890 µg

The residues on both palms of a subject after the hand presses on Days 4 and 5 are estimated as 310 µg and 240 µg of chlorpyrifos, 31 µg and 24 µg of pyrethrins, and 310 µg and 240 µg of piperonyl butoxide.

C. Subject Monitoring

Since chlorpyrifos is a cholinesterase - inhibiting organophosphate insecticide, the American Conference of Governmental Industrial Hygienists recommends monitoring cholinesterase activity in red blood cells (RBC) as an index of biological exposure (ACGIH, 1991). Accordingly, blood samples were collected from each subjec twice (except Dr. Hsu, who declined) at an interval of at least 24 hr prior to Experiment 6, and will be collected once before and after Experiment 7, for RBC cholinesterase activity determination. The ACGIH criterion of post-exposure activity <70% of baseline activity will be used to monitor if excess exposure occurred.

Little reduction in RBC cholinesterase activity is expected in the post-exposure sample. Handwipes of farmers following single mixing/application event show that residues of the applied analyte of 100 μg to 15 mg (n=11) were wiped from both hands (Camann et al., 1993a). However, an RBC cholinesterase drop exceeding 20% was observed in only 30% (3 of 10) farmers who applied organophosphate insecticides at least 10 days over the course of an application season (Potter et al., 1993).

D. Evaluation of Risk

Pyrethrins kill insects by acting as a neurotoxin and causing paralysis. Most humans can metabolize pyrethrins to nontoxic compounds in their liver, rendering harmless this knock down effect seen in insects. There are a very few individuals with a disease known as motor neuron disease or MND. Persons suffering from MND have an incapacity to breakdown pyrethrins through liver enzymatic action (Steventon and Wadding, 1990).

Pyrethrins are used in a synergistic mix with piperonyl butoxide, both in undiluted form, to treat head lice in children. This is one of the most susceptible subgroups of our population and no adverse health effects were reported in a study involving 92 children, both boys and girls, 3 to 15 years of age (Fusia, et al., 1987). The pyrethrin synergistic mixture was applied thoroughly so as to soak the scalp and then allowed to dry for 10 minutes. This treatment was followed by a regular shampooing and combing.

Wester et al. (1984) showed that if pyrethrins and piperynol butoxide were applied to the foreman of individuals in formulated mixtures, the rate of absorption for pyrethrins was 1.9% and for piperonyl butoxide 2.1% judging by a seven day urinary collection following dose application. It is evident from the above facts that neither natural pyrethrins nor piperonyl butoxide pose any adverse health threat to the participants in this experiment.

Chlorpyrifos has been shown to be absorbed through the dermal layer of the forearm at a rate of 3% (Nolan et al., 1984). Chlorpyrifos and its principal metabolites were quickly eliminated and shown to have a low potential to accumulate in the human body. This study also showed that the six healthy male volunteers involved did not show any signs of toxicity nor any depression of plasma or RBC cholinesterase after a single dermal dose of 5 mg/kg.

In Experiment 7, the dried pesticide residue will be wiped from the hands using isopropanol. This solvent is likely to enhance the absorption of the pesticides through the skin.

The maximum dose to subjects will be 27 μg/day of chlorpyrifos, 2 μg/day of pyrethrins, and 18 μg/day of piperonyl butoxide. These estimates are based on conservative, but realistic estimates of the amounts of each pesticide absorbed through the skin of the palm (3% for chlorpyrifos and 2% for pyrethrins and piperonyl butoxide).

The rabbit dermal LD_{50} for chlorpyrifos is 2000 mg/kg (Farm Chemicals Handbook, 1993). This high LD_{50} means there is little chance of an adverse health effect to occur to the subjects in this experiment.

Since all the recognized industrial hygiene organizations (ACGIH, OSHA, NIOSH, MAK) have a skin notation for chlorpyrifos, those participating in this experiment will wash their hands immediately after exposure to the pesticide formulation. The skin notation for healthy workers addresses adverse health effects occurring if a worker comes into contact with pure chlorpyrifos. Industrial and agricultural exposures (Camann, et al., 1993) would be one to several orders of magnitude above what the participants in this experiment will receive.

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SUBJECT CONSENT TO TAKE PART IN A STUDY OF COMPARISON OF TRANSFERS BY THE DRAG SLED, PUF ROLLER, AND HUMAN HAND PRESS OF CHLORPYRIFOS AND PIPERONYL BUTOXIDE FORMULATED MIXTURE RESIDUES FROM SHEET VINYL FLOORING (EXPERIMENT 7)

Southwest Research Institute, Department of Environmental Chemistry, 6220 Culebra Road, San Antonio, TX 78228

We are asking you to take part in a study of the transfer by human hand press of a pesticide formulated mixture residue (chlorpyrifos, natural pyrethrins, and piperonyl butoxide) from vinyl flooring. We want to compare the transfer by hand press to the Dow drag sled and the SwRI PUF roller. We are asking you to take part because you are a healthy adult male employee of the Division of Chemistry and Chemical Engineering who has expressed an interest in being a subject for this study.

If you decide to take part, we will require that you expose the palms of both hands to an estimated total of 1.4 mg chlorpyrifos, 140 µg pyrethrins, and 1.4 mg piperonyl butoxide over three days. The procedure for the study requires each individual's hands be inspected for any cuts, abrasions, or breaks in the skin by Nicholas J. Giardino. Any volunteer with a lesion on his hands will have to wait for it to heal. Hand washing with soap and water will be done prior to and after the hand presses. You will place a vinyl glove on one hand and then do ten presses of the palm of the ungloved hand on an exposed 3 in. x 25 in. strip of the treated vinyl. You will do two hand presses (one with each hand). Each hand press will be done on each of three consecutive days on the carpet that was treated with the pesticide mixture on the first day. After each hand press, you will walk a short distance to an uncontaminated area and wipe your hands with an isopropanol-saturated gauze pad. The total elapsed time for the completion of hand presses and wipes will be approximately thirty minutes each day. We will also require that you perform wipes of both hands after doing hand presses on clean untreated vinyl on two days before the pesticide application. If you are injured as a result of the research procedures, medical care will be provided.

We do not expect you will experience any discomfort during the study. We also expect that no adverse health effects will occur.

Reduced cholinesterase activity in red blood cells (RBC) is one biological indicator of exposure to pesticides (recommended by the American Conference of Governmental Industrial Hygienists). Therefore, as a means of monitoring the condition of your health (ie., keeping your exposure to a minimum) we have arranged to have your blood monitored for RBC cholinesterase activity. Initially on two days before exposure begins and once after the hand press experiments, five milliliter samples will be collected by a registered nurse at the SwRI medical clinic. Blood drawing sometimes involves mild pain, or bruising, and may rarely cause infection at the place of the needle stick.

Consenting to the blood draw involves minimal risk; however, there is a possible benefit to you. In the event that your cholinesterase activity suggests an unhealthy condition of exposure, additional steps will be taken to limit the exposure of you and other subjects in similar future experiments. We do not guarantee that you will benefit from taking part in this study.

SUBJECT CONSENT TO TAKE PART IN A STUDY OF COMPARISON OF TRANSFERS BY THE DRAG SLED, PUF ROLLER, AND HUMAN HAND PRESS OF CHLORPYRIFOS AND PIPERONYL BUTOXIDE FORMULATED MIXTURE RESIDUES FROM SHEET VINYL FLOORING (EXPERIMENT 7)

Southwest Research Institute, Department of Environmental Chemistry, 6220 Culebra Road, San Antonio, TX 78228

Everything we learn about you in the study will be confidential. If we publish the results of the study in a scientific magazine or book, we will not identify you in any way.

Your decision to take part in the study is voluntary. You are free to choose not to take part in the study or stop taking part at any time. If you choose not to take part or to stop at any time, it will not affect your status in the Department of Environmental, Chemistry, Southwest Research Institute.

If you have any questions at any time, contact David Camann at 522-2673. The University of Texas Health Science Center committee that reviews research on human subjects (Institutional Review Board) will answer any questions about your rights as a research subject (567-2351).

We will give you a signed copy of this form to keep.

YOUR SIGNATURE INDICATES THAT YOU HAVE DECIDED TO TAKE PART IN THIS RESEARCH STUDY AND THAT YOU HAVE READ AND UNDERSTAND THE INFORMATION GIVEN ABOVE AND EXPLAINED TO YOU.

SIGNATURE OF SUBJECT:

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SIGNATURE OF WITNESS:

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SIGNATURE OF INVESTIGATOR:

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DATE: __________________ /TIME: __________________