THE DISTRIBUTION OF CHLORPYRIFOS FOLLOWING A CRACK AND CREVICE TYPE APPLICATION IN THE U.S. EPA INDOOR AIR QUALITY RESEARCH HOUSE.

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ABSTRACT
A study was conducted in the U.S. EPA Indoor Air Quality Research House to determine the spatial and temporal distribution of chlorpyrifos following a professional crack and crevice application in the kitchen. Following the application, measurements were made in the kitchen, den and master bedroom over 21-days. Airborne concentrations were collected using both polyurethane foam (PUF) and a XAD/PUF (OVS) media. Measured airborne concentrations were similar for the two samplers, were higher in the three rooms following the application, reached maximal levels 24-h post-application, and declined steadily over the 21-day study period. Spatial and temporal distributions were measured using 10-cm^2 cotton deposition coupons. Sections were cut from existing carpet to determine the total extractable residues. Chlorpyrifos was measured from all matrixes in the kitchen, den and bedroom and shows the transport of airborne residues from the point of application to remote locations in the house.

INDEX TERMS
Chlorpyrifos, Translocation, Pesticide, Residential exposure.

INTRODUCTION
Pesticides are applied in and around human habitations to control a variety of pests and may place toxicants in close proximity to humans. Pesticide residues may translocate from their original points of application following treatment as vapors, bound to particles, or through physical transport processes. The principal factors that influence their movement are the compounds physiochemical properties (i. e., the vapor pressure of the active ingredient and formulation type), the substrate that deposits contact, and the physical activities of humans and pets. Degrading factors such as photolysis and microbial activity less influences pesticide residues found indoors. Furthermore, residues present indoors may persist or accumulate over time and are commonly measured in residential dwellings at concentrations ranging from 10 to 100 times higher than those found out-of-doors (Lewis and MacLeod, 1982). Exposure to indoor pollutants such as pesticides may pose risks to occupants through inhalation, dermal absorption, and direct or indirect ingestion.

A pilot experiment was conducted in the U. S. EPA's Indoor Air Quality Research House to investigate the contribution of a crack and crevice application of the insecticide chlorpyrifos to airborne residue levels in the home. In addition, the deposition of airborne residues onto deposition coupons and indoor carpeting was discussed. Chlorpyrifos is no longer registered for indoor, residential crack and crevice applications. However, these data are relevant to

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understanding the relationships between indoor applications of semi-volatile pesticides and the movement of like compounds in the indoor environment, and the potential for human exposure.

METHODS

The Research Test House

The study reported here was conducted in November 2000, in the U.S. EPA's Indoor Air Quality Research House. The test house is an unoccupied one-story, seven-room (three bedroom), ranch-style house located in a residential neighborhood in Cary, NC (Figure 1). The interior volume of the test house contains a total 293 m^3 with 122 m^2 of living area. All rooms are void of furniture and covered with wall-to-wall pile or shag (den) nylon carpet except the kitchen and the bathrooms. The test house is defined in that air exchange rates, temperature, and relative humidity are continuously monitored. The rooms are open to the entry hallway and the kitchen (Figure 1) and their physical separation is only partial. The kitchen is open to the den via a "pass-through opening".

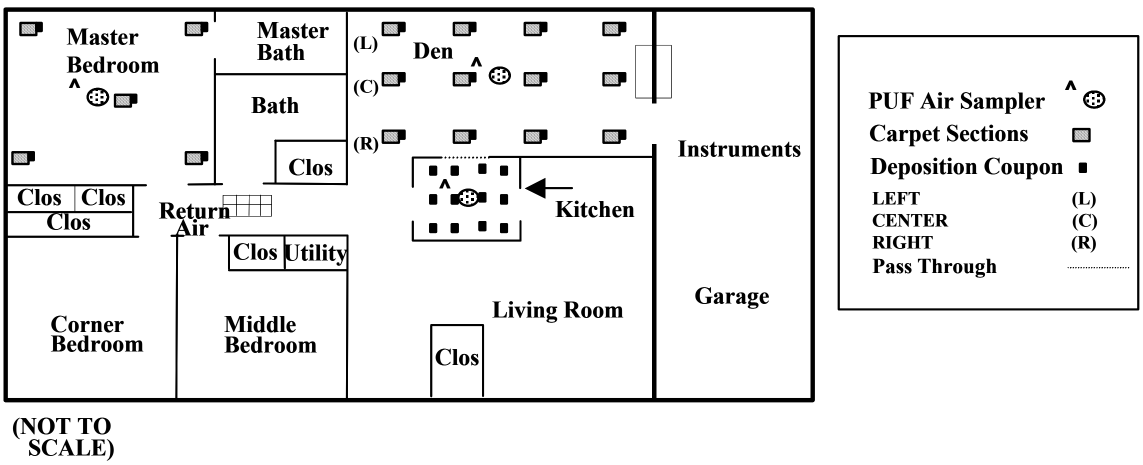

Figure 1. Overview of the IAQ Research Test House with the sample locations shown.

The Pesticide Application

A 0.5% solution of the organophosphate insecticide, chlorpyrifos [O,O-diethyl-O-(3,5,6-trichloro-2-pyridinyl) phosphorothioate], was prepared as per label directions by diluting 78 mL of a commercially available, emulsifiable concentrate formulation with 3700 mL of tap water in a pre-cleaned 1-gallon compressed air sprayer. A total of 259 mL of the finished solution was applied in the kitchen only (Figure 1) theoretically providing 1.29 g of active ingredient applied. A licensed pest control operator using a compressed air sprayer operated at 30 psi and equipped with pin-stream-type spray tip performed the applications. The application simulated a "clean-out" type treatment that is conventional for the control a cockroach infestation. Here the dilute solution is systematically placed into the potential cockroach harborages such as the cracks and crevices of the cabinetry, and around and behind the stove, refrigerator and dishwasher.

Prior to the application, all windows were closed and the furnace fan was turned off. Afterwards, the house thermostat was set to 22 °C (72 °F) for the duration of the experiment. The interior doors remained open throughout the test. Ceiling fans remained off throughout the experiment.

Air Monitoring
Air monitoring was conducted using both commercially available Polyurethane Foam (PUF) tubes and the OSHA Versatile Sampler or OVS tubes (SKC Inc., Eighty-Four, PA). The PUF tube was a 76 by 20-mm PUF plug in glass filter housing. The PUF system was open faced with no particle cutoff inlet. The OVS tube consisted of a 74 by 13-mm glass housing containing a quartz filter and two 140 and 270 mg beds of XAD-2 partitioned between PUF. Both monitors were suspended 100-cm above the floor in the living room, den and the master bedroom (Figure 1). The tubes were connected by Tygon tubing to SKC Universal XR sample pumps. The pumps were calibrated to a flow rate of 3.8 and 1.0 L/min for PUF and OVS, respectively. Air was drawn over the media for a period of 24-h. The sample inlets were directed towards the floor. Samples were collected prior to the application and at days 1, 3, 7, 14 and 21 days post-application. Following sample collection, the PUF and OVS tubes were capped with aluminum foil and individually sealed in plastic bags. The tubes were put in ice chests at reduced temperatures for transport.

Deposition Coupons
Johnson and Johnson Sof-Wick Surgical Sponges (100 cm^2) were used to determine the surface deposition of airborne chlorpyrifos following the application. Each deposition coupon consisted of a surgical sponge backed by solvent rinsed aluminum foil. The deposition coupons were placed on the floor in the kitchen, den, and bedroom (Figure 1) and collected prior to, immediately following the application, and at days 3, 7, 14 and 21 days post-application. At each sampling interval, the deposition coupons were collected and replaced with a new coupon. Coupons were individually collected immediately following the application in the kitchen and den, but were aggregated in the bedroom. At all other sampling intervals, the deposition coupons in the kitchen and den were combined as a single sample by rows across the length of the room, except in the bedroom where all five coupons were combined. The samples were collected using clean, solvent-rinsed forceps, placed in labeled glass jars equipped with Teflon lined lids, and stored in ice chests at reduced temperatures for transport.

Carpet Sections
Prior to the insecticide treatment, groups consisting of six, 16-cm^2 carpet sections were precut in the den and master bedroom (Figure 1). Twelve and five groups were cut from the den and bedroom carpeting, respectively, at locations adjacent to the deposition coupons. Each group of carpet sections remained in place over the course of the study. Similar to the deposition coupons, the carpet sections were collected prior to, immediately following the application, and at days 3, 7, 14 and 21 days post-application. Samples in the den were combined as single samples across rows, while in the bedroom all five samples were combined as a single sample at each interval. The samples were collected using solvent-rinsed forceps, placed in labeled glass jars, and stored in ice chests at reduced temperatures for transport.

Chemical Analysis
The samples were extracted using Soxhlet or shake techniques in a solvent of 5% diethyl ether/hexane. Samples were analyzed using a Hewlett-Packard 5890 gas chromatograph equipped with a liquid auto-sampler and electron capture detector. A DB-5 fused silica column (30 m X 0.25 mm) was used for quantitation. The carrier flow rate was 2.0 mL/min. The temperature program was initiated at 125°C and ramped to 200 °C at 4 °C /min and ramped from to 290 °C at 8 °C /min. The capillary injector was operated in the splitless mode for 1-min. Injector and detector temperatures were 240 and 300 °C, respectively. Instrument calibration was performed using calibration standards containing chlorpyrifos,

decachlorobiphenyl (surrogate) and 2,4,5-tribromobiphenyl (internal). A five-point calibration curve using a quadratic fit was generated across an operating range of 10 to 250 pg/μL.

Other Research Test House Measurements

The air exchange rates were determined by using the tracer gas decay technique. Temperatures were measured in all rooms and outdoors and the relative humidity was measured in selected rooms and outdoors. Meteorological conditions were measured with a system on-site. Data for the environmental measurements were recorded continuously during the study, but are not reported here.

Quality Control

Laboratory quality control included matrix blanks, spikes and duplicates of PUF, OVS, and deposition coupons and carpet sections. Field quality control was similar, but did not include carpet spikes. Chlorpyrifos was not detected from any of the laboratory or field blank samples. Fortified spikes containing 100 ng of chlorpyrifos provided recovery efficiencies (mean ± SD) for field control samples of PUF, OVS, and deposition coupons of 114±12, 103±11%, and 98±8%, respectively. Laboratory control samples of PUF, OVS, deposition coupons and carpet sections fortified at a similar level provided recovery efficiencies of 122±9, 115±12%, 104±11% and 120±6%, respectively.

RESULTS AND DISCUSSION

Airborne Concentrations

Airborne concentrations of chlorpyrifos measured using PUF and OVS samplers agreed well (Table 1). Very low levels of chlorpyrifos were measurable as background. Maximal chlorpyrifos levels were recovered from both type filters at day 1 (24-h following the application) and declined by more than 70% by day 21. Chlorpyrifos was detected in all rooms at each sampling interval at levels above background. Measured levels were highest at the source and declined as the distance from the source increased.

Table 1. Airborne chlorpyrifos residues collected on PUF and OVS samplers following a crack and crevice type application in the IAQ Research Test House.

		Concentration ($\mu g/m^3$)					
Sampler Type	Room	Pre	1[a]	3	7	14	21
PUF	Kitchen		0.79	0.77	0.32	0.22	0.14
	Den	0.003	0.25	0.14	0.09	0.06	0.07
	Bedroom		0.10	0.07	0.06	0.04	0.03
OVS	Kitchen		1.0	0.62	0.34	0.34	0.18
	Den	0.02	0.33	0.15	0.09(0.08)[b]	0.06	0.06(0.05)[b]
	Bedroom		0.09(0.14)[b]	0.06	0.05	0.04	0.03

[a] Air sampling was initiated immediately following the application and monitored continuously for 24-h. [b] The value in brackets represents a field duplicate sample.

Deposition Coupons

Field and laboratory blanks showed no chlorpyrifos and represent pre samples. Chlorpyrifos concentrations measured from deposition coupons in the kitchen immediately following the application were highly variable (Table 2). Concentrations were highest at the floor/cabinetry junction and lowest along the center row. Measurements collected from deposition coupons located in the den were relatively uniform except for two deposition coupons with high levels located along the wall that adjoins the kitchen. Average concentrations (Table 3) measured from the three rooms show a positive contribution of chlorpyrifos from the kitchen (source) onto the deposition coupons in both the den and bedroom. The chlorpyrifos recovered from the deposition coupons in the kitchen and den decreased as the distance from the source increased. In addition, chlorpyrifos measured from the deposition coupons in all rooms similarly declined over time.

Table 2. Chlorpyrifos concentrations measured from deposition coupons in the den and kitchen immediately following a crack and crevice application

		Concentration (μg/100 cm^2)/ Location in Room			
Room	Row	1	2	3	4
Den	Left	0.07	0.09	0.08	0.08
	Center	0.09	0.08	0.07	0.07
	Right	0.24	1.44	0.06	0.07
Kitchen	Left	0.94	17.86	1.77	22.91
	Center	1.19	0.41	0.66	0.66
	Right	0.15	5.88	0.59	5.19

Table 3. Average concentrations of chlorpyrifos measured from deposition coupons in the kitchen, den and bedrooms at intervals following a crack and crevice application.

	Concentration μg/100 cm^2 / Room		
Day	Kitchen	Den	Bedroom[b]
1[a]	4.85 ±7.57[c]	0.20 ±0.39	0.01
3	3.53 ±2.46	0.34 ±0.03	0.13
7	1.48 ±0.46	0.25 ±0.05	0.08
14	0.52 ±0.32	0.19 ±0.04	0.17
21	0.36 ±0.44	0.19 ±0.04	0.55

[a] The samples were collected immediately following the application. [b] The value represents the five samples combined. [c] Values following the concentration represents ± Standard Deviation.

Table 4. Chlorpyrifos measured from carpet sections from three locations in the den and the bedroom following a crack and crevice application in the IAQ Research Test House.

	Location/ Concentration (μg/100 cm^2)			
	Den			
Day	Left	Center	Right	Bedroom[a]
Pre	1.18	9.83	1.72	0.91
1[b]	1.56	3.51	2.71 (3.03)[c]	0.89
3	1.77	7.20	2.38	1.10
7	1.78	11.70	3.22	1.14
14	2.11	7.72	3.40	1.25
21	2.51	4.94	4.31	1.25

[a] The value represents five samples combined. [b] The samples were collected immediately following the application. [c] The value in brackets represents a duplicate field sample.

Carpet Sections

These findings show a higher than anticipated pre-application levels of chlorpyrifos in the existing carpet (Table 4) and a non-homogenous distribution of chlorpyrifos throughout the study. The highest but most variable values were measured from the center of the den. Samples collected from the right and left rows suggest an increase in concentration over time.

Background levels were detected in the bedroom, but increasing concentrations suggest a possible contribution from the application. High background levels were likely from a previous study that examined chlorpyrifos distribution following the activation of total release aerosols conducted in 1993; however, levels may have been associated with intrusion from sources not associated with this application.

CONCLUSIONS

Crack and crevice type applications in current use by pest control operators locate insecticides in cockroach harborage sites and minimize human exposure to the residues. Here chlopryrifos administered to cracks and crevices in the kitchen resulted in airborne vapors and deposition onto non-target surfaces. The high levels measured from the kitchen floor and in the den were likely due to the application factors such as over spray and splashing. Chlorpyrifos, a semi-volatile compound (vapor pressure 1.7×10^{-5} mm Hg at 25 °C), rapidly distributed within the house. Diffusive processes were important in the immediate dispersion from the point of application, but the active HVAC system was also likely a significant factor. Based on the pesticides distribution throughout the house, many exposed surfaces might be contaminated and serve as potential sources for human exposure, particularly children playing on the floor near the point of application. Exposure assessment studies may need to consider translocation processes when monitoring for semi-volatile insecticides. The high values detected on deposition coupons and carpet sections suggest that residues may persist and exposure estimates may need to evaluate the persistence of pesticides following applications indoors beyond 21 days.

Since the inception of this experiment, registrations allowing for the indoor application of chlorpyrifos have been withdrawn. However, these finding are representative of crack and crevice applications of a semi-volatile compound and short-term distribution at the point of application. Pyrethroid insecticides and baits are currently popular in residential pest control. Transport mechanisms, and spatial distributions are expected to be different and may not be represented well by these findings. Further experiments are required examining different application techniques and classes of insecticides to further our understanding of fate, transport and potential human exposure following residential pesticide applications.

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