# Accumulation of Chlorpyrifos on Residential Surfaces and Toys Accessible to Children

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Quantitative examination of major pathways and routes of exposure to pesticides is essential for determining human risk. The current study was conducted in two apartments and examines the accumulation of the pesticide chlorpyrifos in childrens' toys after the time suggested for reentry after application. It has been established for the first time that a semivolatile pesticide will accumulate on and in toys and other sorbant surfaces in a home via a two-phase physical process that continues for at least 2 weeks postapplication. A summation of the above for a 3–6-year-old child yielded an estimated nondietary total dose of 208 µg/kg/day. Potential exposure from the inhalation pathway was negligible, while dermal and nondietary oral doses from playing with toys contributed to 39 and 61% of the total dose, respectively. If children with high frequency mouthing behavior are considered as candidates for acute exposure to chlorpyrifos residues, the estimated acute dose could be as high as 356 µg/kg/day. Routine reapplication of pesticides could lead to continued accumulation in toys and other sorbant surfaces, e.g., pillows, with large sorbant reservoirs, which can become a long-term source of exposure to a child. Estimates of a child's nondietary exposure to chlorpyrifos associated with toys and other sorbant surfaces for a period of 1 week following application appear to be of public health concern, and studies of actual childhood exposure from this pathway are warranted in the home environment. The above information should be used to determine if current procedures for postapplication reentry are sufficient and to evaluate the need for procedures to store frequently used household toys, pillows, and other sorbant objects during insecticidal application. *Key words*: childrens' toys, chlorpyrifos, nondietary exposure and dose, particle deposition, pesticide application, pesticide residuals, semivolatile pesticide, surface wipes, volatilization.

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By far, principal pathways that cause children and adults in the United States to be exposed to pesticides are in the home. Studies have shown that about 90% of all U.S. households use pesticides (*1,2*). It has been estimated that U.S. homemakers and homeowners use roughly 28.5 million kg insecticides and 126.6 million kg antimicrobials annually (*3*). Further, full-time homemakers and young children spend up to 21 hr/day inside the home, with another 2.5 hr inside other buildings or in transit vehicles (*4,5*). Thus, individuals spend up to 90% of their time indoors, which provides the opportunity for significant contact with indoor contaminants such as pesticides. The pesticide chlorpyrifos (*O,O*-diethyl *O*-[3,5,6-trichloro-2-pyridyl] phosphorothioate) has been used more frequently in U.S. homes than other pesticides because it is a broad-spectrum organophosphate insecticide (*6*). Chlorpyrifos gained popularity as a broad-spectrum insecticide in the wake of the decreased availability of compounds such as aldrin, dieldrin, and chlordane.

Because of the potential health significance of high exposures to pesticides, it is necessary to determine how chlorpyrifos, and other pesticides, distribute on and in indoor surfaces after application by homeowners, renters, and professional applicators. Consumer uses of pesticides in and around homes are of special concern because homeowners have access to some of the same chemicals as professional applicators and may use and store these chemicals in a manner that places them and their families at higher risk because of the lack of training or experience in their application. For example, between 1991 and 1992, the San Francisco Poison Control Center reported almost 1,000 adverse health outcomes due to pesticide exposure. Two hundred cases involved children who were 5 years of age or younger (*3*).

Following an application, pesticides deposited indoors can represent a significant source of potential contact and exposure to young children through nondietary ingestion and dermal absorption pathways. Children are of special concern for exposure because of their frequent contact with surfaces that may contain pesticides and their display of enhanced hand-to-mouth activity, which leads to ingestion of the pesticides.

From 1985 to 1990, the EPA conducted the Non-Occupational Pesticide Exposure Study (NOPES) in Jacksonville, Florida, and Springfield, Massachusetts, to assess nonoccupational total human exposures to 32 pesticides and pesticide breakdown products. Their objective was to estimate the distribution of nonoccupational exposures from air, drinking water, dermal contact, and food; however, air monitoring was the primary focus of the study. Homes ($n$ = 216) were sampled for the presence of 32 different airborne compounds, and airborne chlorpyrifos was measured in both locations. In Jacksonville, chlorpyrifos was found in 100% of the household indoor air (*7*).

In addition to indoor air, insecticides can be found on floors and other surfaces and may contribute significantly to the total exposure of the general population. However, there is a paucity of data available for making an accurate assessment of the relative importance of oral (nondietary), dermal, and inhalation exposures to household pesticides (*8–10*).

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Chlorpyrifos and other pesticides are applied for termiticidal treatment in crawlspace and slab-type construction dwellings. They are also applied using crack and crevice treatment for the control of cockroaches. Broadcast applications, however, may present the greatest potential for exposure in a home because a pesticide is applied ubiquitously on large area surfaces, e.g., carpeting (*11*). The technique is still used frequently by homeowners, apartment maintenance personnel, and small pest control operations in the United States and other countries. This paper evaluates nondietary ingestion and dermal contact associated with surfaces and children's toys after treatment of two similar apartments with Dursban (EPA registration no. 464-571). The formulation contained 41.5% chlorpyrifos. The measurements included concentration of chlorpyrifos in air, in toys, and in dust in and on smooth surfaces (*12–14*). The study also documented the time–series distribution of pesticides in various media to elucidate deposition patterns in and on surfaces and to estimate nondietary oral and dermal exposure of children to chlorpyrifos.

## Methods

***Sample collection strategy.*** The study reported here was conducted in two apartment suites located at Rutgers University, Piscataway, New Jersey, during July 1996. The two apartments had identical furnishings and layout and had a living space of approximately 860 $ft^2$. The living room and both bedrooms were carpeted and linoleum was used on all other floor surfaces. The heating, ventilation, and air-conditioning unit (HVAC) in the apartment was an evaporator/cooler system. The HVAC was self contained within each apartment and was operated throughout the study period. Partial ventilation was used in each apartment during the experiment. The windows were kept closed during pesticide application and for 2 hr after application. Following that period, the windows were opened for 4 hr and a fan was operated near a window during this time. Subsequently, the windows were closed and remained closed for the 2-week study period. The partial ventilation scheme was employed because it best represents a situation in which a homeowner applies the pesticide following label directions and provides a period of ventilation after pesticide application.

The pesticide formulation consisted of a 40-ml concentrate (containing 58% inert ingredients) that produced a 0.5% chlorpyrifos solution when added to 1 gal water. Broadcast insecticide treatments were made to the entire floor surface area using a 1-gal stainless steel pump sprayer with a hollow cone nozzle and applied by a licensed pesticide applicator. The application lasted 5–7 min/room, and approximately 2,000 ml of the formulation was used in each apartment. This quantity of pesticide mixture yielded 12 g chlorpyrifos applied to surfaces in an apartment (*15*).

The temperature and relative humidity were recorded for each apartment continuously over the 2-week study period. The temperature ranged from 65 to 77°F ± 3°F standard deviation (SD), and the relative humidity ranged from 59 to 79% ± 5%.

Air, surface, and toy samples were taken as part of the study (Table 1). Based on literature values and a pilot investigation conducted during August 1995, the time periods specified in Table 1 were selected for sampling (*10,16–22*). Air samples were taken in the living area. Surface-wipe samples were taken from the top of a dresser (plastic laminate top) located in one of the bedrooms. Figure 1 illustrates the sampling scheme for wipe samples taken from the dresser top. The boxes labeled A represented regions of accumulated chlorpyrifos deposition for the labeled periods of time. These areas were sampled at the specified time interval, and each was wiped only once during the study. The box labeled R represents a region of repeated wipe sampling. This area was sampled at each post-application time interval. It was used to measure the deposition of pesticide residues between each sampling period. After the first sample was taken, region R contained a hexane–methanol mixture because this mixture was used as a wetting agent for the wipe samples. This is important for comparisons with the chlorpyrifos results obtained from the toys. The sampling scheme provided data to compare the magnitude of surface residues present on areas wiped once (A) and areas wiped repeatedly (R).

Plastic toys called Slammers (Imperial Toys, Ltd., China) and plush toys filled with polyfill called Geoffrey (Toys "R" Us, Inc., Paramus, NJ) were placed within prepared grids on the living room floor 1 hr after chlorpyrifos application, and one of each toy was removed for analysis of chlorpyrifos uptake at 8, 24, 72, 168, and 336 hr after application (for a total of five versions of each toy). These items and their time of removal represented a situation in which a toy was placed and left in a pesticide-treated room and sequentially removed after the period of time recommended by manufacturer labels for safe reentry. The toys were not directly sprayed with the pesticide. The measurement results from the deposition of chlorpyrifos on the toys were compared with the R surface samples.

***Sampling techniques and analytical methods.*** The indoor air samples were collected with a low flow rate indoor air sampling impactor (IASI) with a $PM_{10}$ inlet (to collect particles of ≤10 µm in diameter) (*12*). The filter was a rough cotton linter paper impregnated with activated carbon and had a thickness of 0.40 mm. The samples were collected for a period of 12 hr. The filters were extracted in 10 ml toluene and were sonicated in an ultrasonic bath (Ultrasonic Bath BS-131-6, 60 Hz; Sonic Systems, Inc., Newtown, PA) for 30 min. An aliquot was pipetted into 1.2-ml amber glass auto sampler vials and subjected to gas chromatography (GC) analysis.

The Lioy-Weisel-Wainman (LWW) sampler (Patent #RWJ-91-28) was employed to measure the surface loading (micrograms per square centimeter) of dust and pesticides on surfaces (*13,14*). The LWW sampler used a template to mark a specific area (100 $cm^2$) for the quantitative collection of dust by movement of a constant pressure block within the template. A self-adhesive gray silicone rubber pad was attached to the smooth side of the block. The filter media used were Empore Carbon-18 disks (3M, Minneapolis, MN), which are traditionally used for analysis of waste water. Tests demonstrated 99–117% recoveries for chlorpyrifos at three spiking levels. Prior to sampling, the filter was immersed in methanol for approximately 2 sec and was followed by immersion in hexane for the same amount of time. Care was taken to shake off excess solvent against the sides of the solvent retainer (an aluminum weighing dish, for example). The filter was placed on

**Table 1.** Sampling times and solvents for sample media

| Sample type | Sampling times after application (hr) | Extraction solvent |
|---|---|---|
| Toys | 8, 24, 72, 168, 336 | Hexane |
| Air | 12, 36, 48, 60, 72, 168, 336 | Toluene |
| Surface | 4, 8, 12, 24, 36, 48, 60, 72, 168, 336 | Hexane |

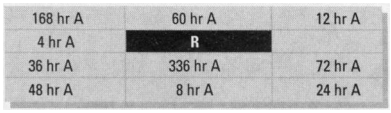


**Figure 1.** Chlorpyrifos residual sampling grid for a dresser top during a 1–336 hr period after application. Abbreviations: A, surface residues from single wipes; R, surface residues from multiple wipes.

the rubber pad, and the sampling block with the filter were moved back and forth five times across the length of the template. A total surface area of 100 $cm^2$ was wiped using the LWW sampler as a template. The filters were extracted with 5 ml hexane (Optima grade, Fisher Scientific, Norcross, GA) and sonicated in an ultrasonic bath for 30 min. The extract was split into two aliquots per wipe sample. An aliquot was pipetted into 1.2-ml amber glass auto sampler vials and subjected to GC analysis.

The toys were weighed prior to being placed in the rooms. The plastic toys were extracted in 20 ml hexane and the plush toys were extracted in 180 ml hexane. Both extracts were sonicated for 30 min. Following sonication, the extract from the plush toys was subjected to rotary evaporation (Buchi Rotavapor R-114, Brinkmann Instruments, Inc., Westbury, NY). The extract was evaporated to dryness and placed in 5 ml hexane. An aliquot was pipetted into 1.2-ml amber glass auto sampler vials and subjected to GC analysis.

All sample aliquots were kept frozen at -15°C until analysis by GC. Capillary gas chromatography with an electron capture detector (GC/ECD) was used to detect chlorpyrifos in the sample extracts. A Hewlett-Packard Gas Chromatograph 5860 Series II (Hewlett-Packard, Wilmington, DE) equipped with an HP Nickel 63 Electron Capture Detector and an Autosampler Injector 7673 was used to measure the concentration of chlorpyrifos in all samples. Quantification was performed using HP ChemStation chromatography software (Hewlett-Packard). A split/splitless injector was held at 200°C, and a 30-m (0.32 mm inner diameter DB-1701) fused silica capillary column, 0.25 µm film thickness (J & W Scientific, Folsom, CA) was temperature programmed from 33°C (held for 1 min) to 163°C at 30°C/min, from 163 to 253°C at 5°C/min, and held at the final temperature of 253°C for 15 min. The detector temperature was held at 300°C. The carrier gas (helium) flow rate was 1.5 ml/min and the flow rate of the make-up gas (nitrogen) was 30.7 ml/min. The injection volume for all samples was 1 µl. Solvent blanks were included with every run set. Duplicate sample analysis was completed on every tenth sample, and a 5% relative SD in the concentration was considered acceptable between duplicates. Chlorpyrifos standards were prepared by making a stock solution of 1,000 µg/ml by dissolving 25 mg of the reference standard in 25 ml hexane. This solution was serially diluted to produce standard solutions containing chlorpyrifos at 0.04, 0.08, 0.1, 0.3, 0.5, and 1 µg/ml. A calibration curve was generated by plotting the area response against the amount. The resulting regression equation was used for all pesticide determinations.

## Results

Chlorpyrifos concentrations measured on the A surfaces, presented in Figure 2, peaked 36 hr postapplication at 43 ng/$cm^2$. Subsequently, the levels decayed with time as the chlorpyrifos either degraded or volatilized from the surface. In contrast, the repeat wipe samples taken from region R decreased slightly after the 36-hr peak, but began to increase again after 72 hr. The concentration of chlorpyrifos in region R was equal in magnitude to accumulated residues (region A) at sampling times less than 72 hr, and was at least twofold higher than region A at 168 and 336 hr after application. The vapor pressure of chlorpyrifos is reported to be $1.87 \times 10^{-5}$ mm Hg at 20°C, which makes it a semivolatile organic compound. Semivolatiles can partition between the vapor phase and condensed phase; thus, a fraction of chlorpyrifos in the deposited dust will be released into the gas phase and a fraction will remain sorbed to the deposited particles (*23*). This contradicts the commonly accepted paradigm of pesticides being only a residue.

The two-phase process is illustrated in Figure 2. Chlorpyrifos is first distributed in the particle phase (Phase 1) immediately following application. Then, over time, chlorpyrifos gradually volatilizes (as shown by the decrease in the region A values) into the room (Phase 2). Subsequently, the vapor can be sorbed to an activated surface, such as on the dresser (Region R) that had been wiped repeatedly with the hexane–methanol mixture. The volatilization process also is supported by data collected in a study conducted by Bukowski et al. (*15*), in which they used experimental conditions similar to those described in the methods section, except that the apartment windows were kept closed throughout their study. A passive dosimeter employed during that study obtained time-weighed average inert volatile organic compound (VOC) measurements during the 24-hr period following the application. The measured levels peaked at 12 hr after application, which was considerably later than would be predicted by EPA reentry models (2–4 hr) (*24*). Such (re)volatilization into a room would occur for the semivolatile chlorpyrifos, except at a slower rate than would be expected for the VOCs.

Once the chlorpyrifos is in the gas phase, it can diffuse into a medium possessing sorptive properties, which should be the case for the two different types of toys placed on the floor after pesticide application. When the time course of chlorpyrifos residual accumulation was examined in each type of toy, it was observed that the pesticide did sorb to the plastic and the felt toys (Fig. 3), with both showing significant increases in chlorpyrifos levels. The levels on the plastic toys increased rapidly, while the felt toys showed slower but sustained increases in chlorpyrifos levels over the 2-week sampling period. The accumulation of chlorpyrifos on toys was analogous to sorption of chlorpyrifos on the hexane–methanol mixture-extracted dresser surface. The result implies that toys, and especially felt toys, can serve as major sinks and then as reservoirs for particle-bound and vapor phase-bound pesticide residues.

To compare the deposition on the toys with other surfaces, the surface area of the toys was measured prior to placement in the apartments; this showed that the surface concentration of the plastic toys

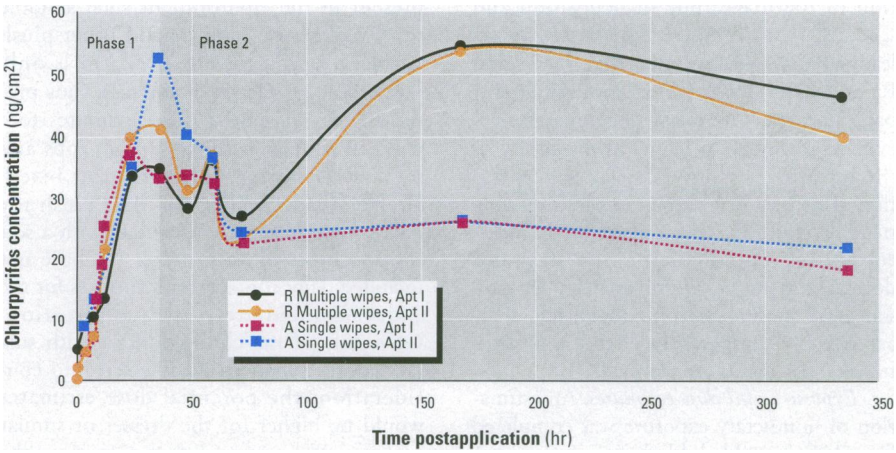


**Figure 2.** Chlorpyrifos surface residues sampled from dresser tops post application in two apartments for two sampling strategies. Wipes for R were hexane–methanol-extractable wipes. Phase 1 is dominated by deposition, and Phase 2 is dominated by volatilization.

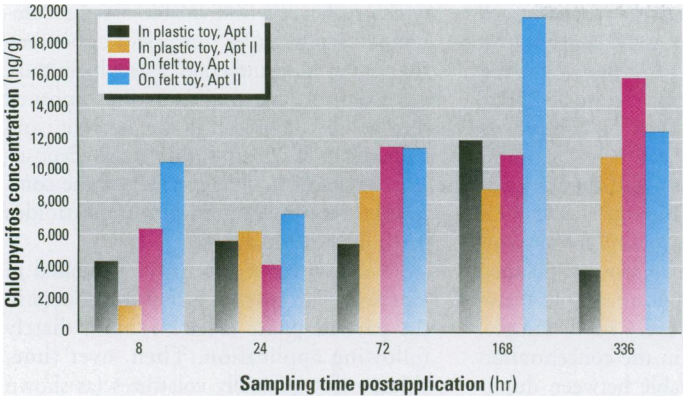


**Figure 3.** Accumulation of chlorpyrifos residues in plastic and on felt toys in two apartments (Apt I and Apt II).

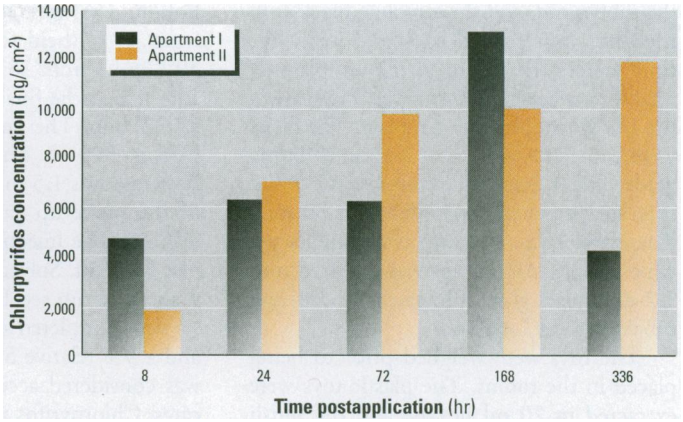


**Figure 4.** Chlorpyrifos surface loading on plastic toys in two apartments.

increased with time and peaked at 1 week after application on an average of 11,503 ng/cm$^2$ (Fig. 4). The chlorpyrifos levels on the toys were two orders of magnitude greater than the loadings (nanograms per square centimeter) found on the surface of the dresser. These results demonstrate that there are numerous sorptive sites for the pesticide to be adsorbed and absorbed by the polyethylene toy (Slammer). The wipes taken from the dresser were representative of the fraction of chlorpyrifos adsorbed by hexane–methanol on or below the surface.

***Simulation of two-phase process of deposition and volatilization.*** On review of the data presented in Figure 2, the initial deposition rate of chlorpyrifos after application and the subsequent volatilization rate of chlorpyrifos were estimated using a first order model described by the equation

$$\frac{dP_s}{dt} = k_1 \times C \times A - k_2 \times P_s, \qquad (1)$$

where $P_s$ = pesticide amount on surface (grams), $k_1$ = deposition rate constant (grams per hour), $C$ = concentration in air (grams per cubic meter), $A$ = area of surface (square meters), and $k_2$ = volatilization rate constant from surfaces (grams per hour).

The equation was solved using Simusolv software (Dow Chemical Corporation, Midland, MI), and $k_1$ and $k_2$ were estimated using maximum likelihood with a constant variance error model. The indoor air concentrations used to estimate $k_1$ and $k_2$ were obtained by linear interpolation of the concentrations measured in the apartments. The actual pesticide profile in air was not modeled because our data set suggests that the rate of volatilization is dependent on additional factors such as temperature. The deposition rate ($k_1$) was estimated to be 7.3 g/hr and the volatilization rate ($k_2$) was estimated by the model to be 0.11 g/hr for the dresser surface (plastic laminate). The resultant surface loading profile for chlorpyrifos is shown in Figure 5. The first order model presented here provides a rough approximation of the magnitude of deposition and secondary volatilization. The latter process leads to accumulation on artificially (region R) and naturally activated surfaces or sorbant surfaces. The effect of temperature is evident in Figure 6 from the similarity of the measured chlorpyrifos air concentration–time profile and the temperature–time profile. The air concentration in both rooms increased during the day and decreased at night. Unfortunately, the present data are too sparse to adequately characterize the temperature effect, and additional experiments are planned.

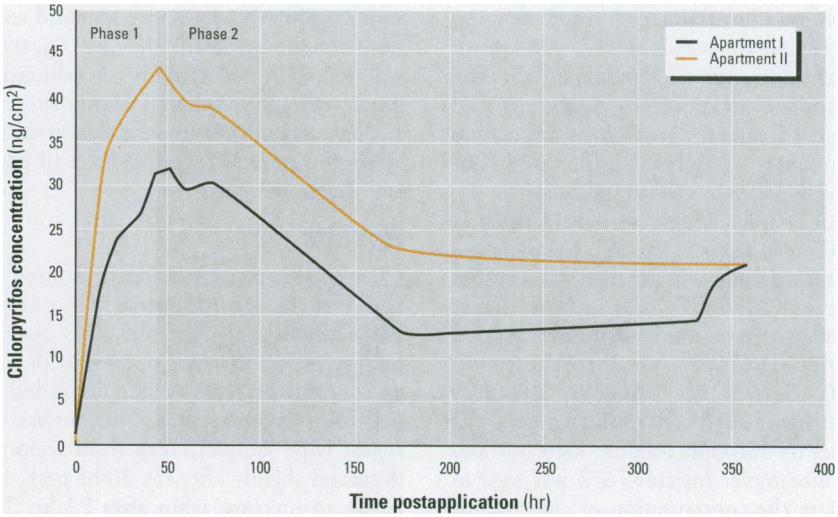


**Figure 5.** Simulation of surface loading of semivolatile organic compounds—chlorpyrifos deposition and volatilization over a 2-week period. Phase 1 is dominated by deposition, and Phase 2 is dominated by volatilization.

***Exposure and dose estimates.*** An estimation of nondietary exposure was completed for a 3–6-year-old child playing in a room 1 week after a broadcast application of chlorpyrifos for inhalation, dermal, and nondietary ingestion. The exposure assessment presented here is derived from chlorpyrifos concentrations on laminated dresser tops and toys (plastics and plush) 1 week after pesticide application. Multiple surfaces are present in the environment such as table tops, mattresses, pillows, and other plush surfaces. Our exposure scenario is only directed at contact with surfaces, thus presenting the potential dose estimates to a child in contact with the dresser tops and toys upon entering the environment 1 week after pesticide application. The plush toy data is used to represent contact with a soft toy and other plush surfaces. We have not included daily contacts with surfaces for the 7 days immediately after application. Obviously, if the child's contact with surfaces during that period is taken into consideration, the potential dose estimates would be higher for the dresser or similar surfaces. We assumed that each time the child touched the dresser top or a toy, he/she was able to extract the same amount of chlorpyrifos residue with each successive

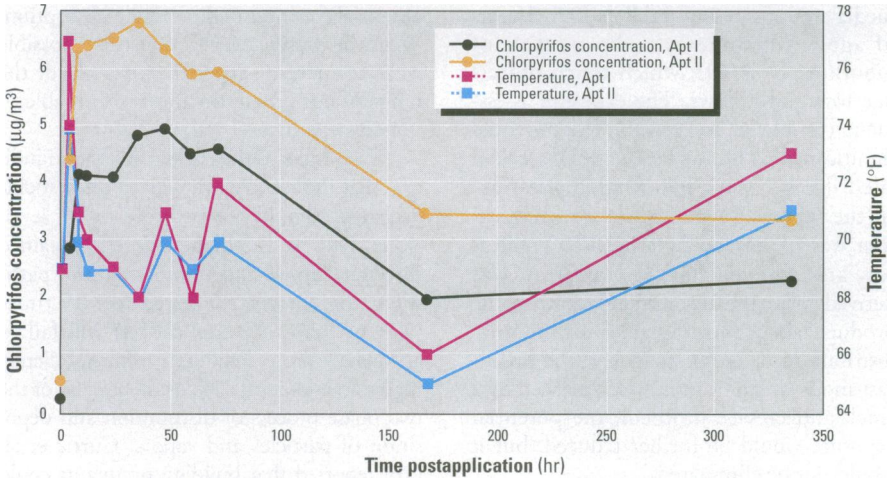


**Figure 6.** Profile of indoor air levels of chlorpyrifos and associated temperature profile for two apartments (Apt I and Apt II).

**Table 2.** Estimated nondietary total chlorpyrifos dose for a child (3–6 years old) living and playing at home 1 week after application

| Route of exposure | Air (µg/kg/day) | Surface (µg/kg/day) | Plastic toy (µg/kg/day) | Plush toy (µg/kg/day) | Dose/route (µg/kg/day) | Percent of total dose |
|---|---|---|---|---|---|---|
| Inhalation | 1.6 | – | – | – | 1.6 | Negligible |
| Dermal | – | 9.2 | 69 | 1.8 | 80 | 39% |
| Oral | – | 21 | 44 | 61 | 126 | 61% |

The human no observable effect level = 30 µg/kg/day (*42*).

**Table 3.** Estimated low nondietary chlorpyrifos dose for a child (3–6 years old) living and playing at home 1 week after application

| Route of exposure | Surface (µg/kg/day) | Plastic toy (µg/kg/day) | Plush toy (µg/kg/day) | Dose/route (µg/kg/day) | Percent of total dose |
|---|---|---|---|---|---|
| Dermal | 3.1[a] | 23[a] | 0.61[a] | 27 | 42% |
| Oral | 6.2[b] | 13[b] | 18[b] | 37 | 58% |

[a]Dermal absorption assumed to be 1%.
[b]Oral absorption assumed to be 30%.

**Table 4.** Estimated high nondietary chlorpyrifos dose for a child (3–6 years old) due to frequent hand to mouth and/or surface activity at home 1 week after application

| Route of exposure | Surface (µg/kg/day) | Plastic toy (µg/kg/day) | Plush toy (µg/kg/day) | Dose/route (µg/kg/day) | Percent of total dose |
|---|---|---|---|---|---|
| Dermal | 34[a] | 69 | 1.8 | 105 | 29% |
| Oral | 146[b] | 44 | 61 | 251 | 71% |

[a]Derived from observational data for hand–surface touches of 366 times/hr (*28*).
[b]Derived from observational data for hand–mouth touches of 70 times/hr (*28*).

contact. This is a reasonable assumption because there are 1) numerous surfaces present in the environment, 2) multiple areas for contact on the same surface or toy, and 3) children come into contact with multiple surfaces during the day. Other assumptions made to calculate potential dose include 1) inhalation rate = 12 $m^3$/day (*25*); 2) body weight = 20 kg (*25*); 3) surface area of both hands = 400 $cm^2$ (200 $cm^2$ for area of fingers); 4) 3% dermal absorption of chlorpyrifos (see Table 2) (*26*) and 1% dermal absorption (Table 3); 5) 100% absorption through inhalation and oral pathways (default assumption) (Table 2, Table 4) and 30% oral and 1% dermal absorption (Table 3); 6) 75% of residues transferred from surface to hand (*27*); 7) 100% transfer of residues from toy to hand, and 10 plastic toys' and 3 plush toys' surfaces contacted with once a day; and 8) surface area of a plastic toy = 7.73 $cm^2$ and surface area of a plush object = 396 $cm^2$.

The estimated absorbed inhalation dose, a product of air concentration, inhalation rate, and percent absorbed, divided by body weight was 1.6 µg/kg/day at 1 week after application (Table 2). The dermal dose (based on touching a flat surface, a product of surface concentration, the percent transferred and absorbed, the surface area of the hand, and the frequency of hand to smooth surface touches, divided by body weight) was estimated to be 9.2 µg/kg/day. The number of hand to surface touches was derived from direct observations based on 8 hr activity per day and was obtained by videotaping young children (*28*). An absorbed dermal dose derived from playing with a hard plastic toy, a product of concentration on the toy surface, percent transferred and absorbed (3%/case), surface area of the hand, and the number of toys played with once a day, divided by body weight, was estimated to be 69 µg/kg/day. Similarly an absorbed dose derived from playing with a plush object was estimated to be 1.8 µg/kg/day. The nondietary absorbed oral dose associated with touching a surface followed by insertion of the hand into the mouth, a product of surface concentration, the percent absorbed, the surface area of a child's fingers, and hand to mouth touches, divided by body weight, was 21 µg/kg/day. The frequency of hand to mouth touches was also derived from direct video observational data (*28*). The oral dose (100%/case) associated with inserting a toy into the mouth and chewing on the material, a product of concentration on the toy surface, percent sorbed onto the area of the toy in contact with the child, and the number of times the toy is played with once a day, divided by body weight, was estimated to be 44 µg/kg/day for the plastic toy and 61 µg/kg/day for the plush object.

A summation of the above for a 3–6-year-old child yielded an estimated nondietary total dose of 208 µg/kg/day (Table 2). Potential exposure from the inhalation pathway was negligible, while dermal and nondietary oral doses from playing with toys contributed to 39 and 61% of the total dose, respectively. If children with high frequency mouthing behavior are considered as candidates for acute exposure to chlorpyrifos residues, the estimated acute dose could be as high as 356 µg/kg/day (Table 4). This calculation employs the same values for all other variables used to calculate Table 2.

The EPA has suggested that 3% dermal absorption of chlorpyrifos may be high. Similarly, the assumption of 100% absorption through the oral pathway may also be high. This calculation was presented to provide a direct comparison with the dose calculated in previous work performed by Fenske et al. (*10*). Table 3 illustrates the potential nondietary doses obtained when a 1% dermal absorption and 30% oral absorption are used in the calculation. With the latter assumptions, the total nondietary dose estimate was 64 µg/kg/day. In either case, however, results suggest that it is plausible for children to accumulate

body burdens of pesticides in a residential setting where pesticides are routinely used to control insects.

## Discussion

Chlorpyrifos deposited on and in toys and other absorbent surfaces following a typical broadcast application and reentry period were found at levels that could yield substantial doses to a child playing in the treated residence. Chlorpyrifos or other semivolatile pesticides are of special interest because the analyses of the above data show that a significant fraction of such compounds can be distributed to surfaces available to children over a 2-week period. The modeling analyses indicate that deposition occurs by both the gas and particle phase processes. The vapor pressure of chlorpyrifos and the temperature of the ambient environment appear to determine the distribution of the material between the gas phase and the particle phase, and the vapor phase can deposit in or on surfaces by absorption or adsorption, respectively (*23*). The application of the pesticide is followed by a period of equilibrium between the particle and vapor phases. The results indicate that after a period of time, chlorpyrifos is released from the particles into the ambient air of an apartment (residence). This vapor is sorbed onto available surfaces such as polyethylene toys and our artificially activated plastic laminate dresser top, a phenomenon previously unaccounted for in estimates of a child's exposure and risk to pesticides. The pestcide on the laminated dresser top displayed enhanced deposition on previously sampled areas because the hexane–methanol mixture provided sorptive sites for chlorpyrifos vapor deposition. The phenomenon indicates that a variety of common household surfaces, which are filled with foam, e.g., toys, pillows, and bedding, can sorb chlorpyrifos as a result of this two-stage process. Camann et al. (*29*) reported that polyurethane foam (PUF) in furniture, pillows, and mattresses could be contributing sources to indoor air levels of chlordane, chlorpyrifos, dieldrin, heptachlor, and pentachlorophenol. PUF has been used for air sampling of pesticides (*30*). The pesticide accumulation in toys, specifically soft plush toys, as shown by this study indicates that they behave in an analogous manner to PUF and may be a source of pesticides that leads to exposure in young children. The toys can serve as reservoirs of accumulated chlorpyrifos levels (adsorbed and absorbed) over the 2-week period. The bioaccessibility of the pesticide sequestered in the toy was not addressed in this study and is an improtant follow-up experiment.

The population at greatest risk of exposure to pesticides found indoors in various media are infants and toddlers (0.5–5 years of age); this appears to be a result of mouthing of hands, which touch objects like toys and pillows. The exposure assessment completed to examine the potential significance of nondietary pathways calculated doses 1 week following application. In the reported experiments, the application was performed by a licensed applicator, and the ventilation condition was derived from the recommendation on the product label (both designed to minimize distribution of the pesticide). If the broadcast mode of application were replaced by a crack and crevice protocol, the potential exposure would be further reduced, but it would not be eliminated.

Some of the uncertainty associated with our exposure estimates was removed by the use of actual time–activity data. The direct counts for hand to surface and hand to mouth touches enable a more realistic approximation of potential exposure of a child to pesticide residues. It has been suggested that a 3% dermal absorption rate for chlorpyrifos might be low (*9*); however, others have suggested that these values are high. The EPA used a 1% absorption rate in the analyses of exposure presented in Table 3, based on a study conducted by Nolan et al. (*26*). However, the hands of young children are often moist with either saliva or sweat, and it has been reported that saliva-wetted hands transferred about 100 times more dried pesticide residues from treated carpet than dry hands (*31*). Thus, young children may transfer and absorb even higher amounts of pesticides when their sticky, saliva-wetted hands contact contaminated surfaces, e.g., toys, plush objects.

In calculating the potential dermal dose from the child's playing with the toy, it was assumed that the child did not wash his/her hands over an 8-hr period. The literature indicates that washing skin with soap and water does not completely remove pesticides (*32*). Further, in the same study it was reported that skin penetration increased with residence time of the pesticide on skin for most compounds. Fenske and Lu (*33*) reported that the recovery of chlorpyrifos from hand rinses was, at the most, 54% after a known amount of the pesticide was transferred to the hand. This incomplete removal of the pesticide from hands may allow pesticides to persist for days after exposure and to increase with repeated contact. Wester and Maibach (*32*) reported that malathion exhibited greater percutaneous absorption with increased residence time on the skin due to the binding of the pesticide by all skin layers. Longer durations of skin contact time and occlusion, e.g., clothing, enhanced the potential for increased pesticide absorption. With the presence of each of these possible ways to increase exposure for a child, the range of our dose estimates is reasonable, if not conservative.

The results of the current study also indicate that the reentry times listed on pesticide packaging should not be based on air levels alone. Because the highest dose is obtained through dermal and nondietary oral pathways, the current suggested reentry times (1–3 hr following application) will fail to adequately protect children from nondietary ingestion and dermal exposure because of the two-phase process of distribution and deposition of particles and vapors. Currie et al. (*16*) reported that building occupants could return to their offices 1 day after treatment with chlorpyrifos. The concentration of chlorpyrifos was roughly one-eighth the threshold limit value (TLV; 200 $\mu g/m^3$) 4 hr after treatment, and it fell to one-tenth the TLV by 24 hr after treatment. The offices were unventilated, and reentry into the rooms was suggested as being safe based on air levels measured over a 10-day period. The exposure analyses for the present study suggests that accumulation of chlorpyrifos in children's toys and other plush objects is of concern for public health and that these objects must not be stored in an open room for at least a week after a single application. Further research is necessary, however, to obtain a distribution of exposure and patterns of contact in order to evaluate new procedures for application and establish appropriate times for reentry of individuals and their possessions. For example, the pesticide product labels direct the consumer to avoid reentry until sprays have dried; however, these generic instructions fail to safeguard against chronic exposure to pesticides. On examination of a consumer product containing chlorpyrifos (Raid, S.C. Johnson & Son, Inc., Racine, WI), it was noted that the label cautioned children and pets from contacting treated areas that appeared wet. As shown in our study, areas and surfaces not directly treated with a pesticide are equally prone to pesticide contamination and accumulation.

Wallace et al. (*34*) reported measurable air levels of chlorinated pesticides such as aldrin and dieldrin in a residence 7 years following initial measurement. Other studies have noted the persistence of pesticides in carpets (*35–37*). In a study by Richter et al. (*38*), diazinon, an organophosphate similar in characteristics to chlorpyrifos, was found on the walls of a residence at 12.6–105 $ng/cm^2$. The inhabitants experienced symptoms such as fatigue, nausea, dizziness, headaches, and heaviness in the chest. The maximum cholinesterase depression measured was 21.6% below baseline

levels of cholinesterase, which was measured 15 months after the initial measurement. In our study, the surface loading of chlorpyrifos ranged from 3.6 to 54 ng/cm$^2$ on the dresser top and from 1,950 to 7,075 ng/cm$^2$ on plastic toys, indicating that the potential exposure of children can be substantial in recently or repeatedly treated homes. Thus, a long-term consequence of leaving toys out in rooms routinely treated with pesticides, such as those used in our study, could be an accumulation of high levels of pesticides in toys and other plush objects made with polyurethane foam.

Pesticide exposure to young children will be underestimated if chronic exposures from dermal and nondietary ingestion from contact with pesticides in toys and other furniture are not considered. The reported experiments did not include the contribution of dietary exposure to pesticides. Previous studies have suggested that many of the pesticides applied to food crops in this country are present in food in trace amounts (*4,7,39*). Thus, families that routinely use pesticides can obtain cumulative chronic dietary and nondietary exposures which will increase the body burden of pesticides in children to values above current reference dose (RfD) of 3 µg/kg/day [based upon a no observable effect level (NOEL) of 30 µg/kg/day], the dose of a chemical at which there were no statistically or biologically significant increases in frequency or severity of adverse effects seen within an exposed population and its appropriate control (*40,41*). The estimated dose is also above the allowable daily intake (ADI) for residential exposures, 10 µg/kg/day, which is based upon a NOEL for plasma cholinesterase depression of 100 µg/kg/day (*42*). When the 1% dermal absorption and 30% oral absorption estimates were used, the total nondietary dose of 64 µg/kg/day still exceeded the current ADI by a factor of 6 and the RfD by a factor of 21. The health effects that may result from the range of doses described above are unknown. Thus, issues surrounding the risk–benefit analysis of indoor pesticide applications must be evaluated to determine the need for sequestering toys before, during, and after an application. The high exposure estimate also suggests that, in some cases, acute residential exposures may be substantial and, at a minimum, warrant further research and a thorough evaluation of household exposure/biologically effective dose for the above pathway.

## Conclusions

Surfaces inside residences, such as furniture and toys, can serve as reservoirs for pesticides. The accumulation of semivolatile pesticides in such objects follows a two-stage process whereby chlorpyrifos, the pesticide examined in this study, is initially attached to a particle released during application and deposited on a surface. Subsequently, it is released from the surface as a vapor and is eventually sorbed by furniture and toys. Current suggested reentry times fail to adequately safeguard young children from exposure due to their play time with toys, contact with other plush objects, and frequency of mouthing behavior. The study implies that toys should be stored during the application and for many days after application to reduce the available residue on toys during play and to prevent significant exposures to pesticides by this nondietary pathway. Research in support of a thorough risk–benefit study must be conducted to identify the need for recommendations that can limit toy contact with pesticides and reduce the potential for chronic doses above an RfD or an ADI. This is essential to ensure that children continue to be protected from consequences of insect infestations, but at the same time minimize long-term exposures and potential risks from pesticide accumulation in their toys and play environments.

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