ESTIMATION OF EXPOSURE OF PERSONS IN CALIFORNIA TO PESTICIDE PRODUCTS THAT CONTAIN CHLORPYRIFOS

by

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HS-1661 June 7, 1993

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ABSTRACT

Chlorpyrifos has been used extensively in California to control pests in both agriculture and non-agriculture which amounted to 2.1 million pounds of active ingredient in 1991. Structural pest control consumed about 33% of the total use, whereas major uses in agriculture (about 47%) were in alfalfa, almonds, cole crops, cotton, oranges, and sugar beets. There were 365 illnesses attributed to the use of chlorpyrifos between 1982 to 1989. The major metabolite of this chemical in animals and man is 3,5,6-trichloropyridinol. Exposures expressed as seasonal average daily dosage (ug/kg/day) are 0.36 to 4.1 for applicators, 131 for mixer/loaders, 1.34 to 29.5 for mixer/loader/applicators, and 2.6 for greenhouse applicators. Lower exposures (0.05-2.16 ug/kg/day) were observed for workers conducting cultural practices, cotton scouting and tree fruit harvesting. For indoor exposures, absorbed daily dosages (ug/kg/day) range from 33-40 for infants and up to 17.5 for adults. Chlorpyrifos has been known to inhibit plasma, brain, and red blood cell cholinesterase in experimental animals and man. Chlorpyrifos is in risk assessment because of low NOEL observed for cholinergic signs and because it was put into reevaluation over concerns about excessive indoor exposure potential.

This report was prepared as Appendix B to the Department's Risk Characterization Document for chlorpyrifos.

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APPENDIX B

California Environmental Protection Agency
Department of Pesticide Regulation
Worker Health and Safety Branch
Human Exposure Assessment

Chlorpyrifos

June 7, 1993

INTRODUCTION

Human exposure assessment provides essential information for the risk assessment of pesticides in the registration and reevaluation process. This document will be incorporated as Appendix B in the risk characterization document of the Department of Pesticide Regulation (DPR). It will also be used as a basis for mitigation proposals if exposures to chlorpyrifos are found to cause excessive risk.

Mixer, loader, and applicator exposure estimates were derived from patch or other passive dosimeters. Exposure of harvesters who come in contact with foliage was estimated from dislodgeable foliar residue with an appropriate transfer factor. Inhalation and dermal exposures were used to determine absorbed daily dosage. Indoor exposure estimates were made following exposure of adults to treated carpet under reproducible conditions of contact.

In addition to exposure estimates, presentation of other properties of chlorpyrifos are necessary for a better understanding of its nature, usage and effects. These additional categories are: physical and chemical properties, U.S. EPA status, formulations/precautions, usage, worker illness/injury, dermal toxicity and eye irritation, dislodgeable foliar residues, dermal absorption, and animal metabolism.

PHYSICAL AND CHEMICAL PROPERTIES

Chlorpyrifos, *O,O*-diethyl *O*-(3,5,6-trichloro-2-pyridyl)phosphorothioate, is a colorless solid (molecular formula $C_9H_{11}Cl_3NO_3PS$; CAS # 2921-88-2). It is an insecticide that is widely used in California in and around homes as well as in agriculture. Some physical properties of chlorpyrifos are listed below (Anon., 1986; Packard, 1987):

Melting point (^{o}C)	42-43.5
Water solubility (ppm)	1.4
Octanol/water partition coefficient	50125
Vapor Pressure (mm Hg at 25 ^{o}C)	0.00002

U.S. EPA AND DPR STATUS

Chlorpyrifos was first registered in the United States in 1965. In 1984, the United States Environmental Protection Agency (U.S. EPA) issued a guidance for the reregistration of pesticide products containing chlorpyrifos. Based on the evaluation of the available data, the U.S. EPA allowed continued registration, and chlorpyrifos was not placed under the special review process at that time (U.S. EPA, 1984). Currently, U.S. EPA is in the process of issuing a data call-in for chlorpyrifos. A regulatory decision will be made upon the completion of the review of these data (Edwards, 1991).

Chlorpyrifos has been under reevaluation in the Department of Pesticide Regulation (DPR). The reevaluation was commenced on June 27, 1985 for chlorpyrifos products that were labeled for indoor use. The reevaluation was initiated based on theoretical estimates by the California Department of Health Services (CDHS), assessing the hazards from pesticide absorption from surfaces. The purpose of the reevaluation was to make a risk assessment of the acute hazards of indoor uses of chlorpyrifos (Jones, 1985).

FORMULATIONS/LABEL PRECAUTIONS

Formulations

Registered chlorpyrifos products in California are mostly formulated as liquids (89 products), emulsifiable concentrates (93 products), or aerosols (101 products). There are also 40 chlorpyrifos-impregnated products and 6 products formulated as dusts. Other chlorpyrifos formulations include wettable powders, soluble powders, granulars, and foggers (Pesticide Registration Branch, 1993). The number of registered products of a formulation does not necessarily reflect the trend of use. Some products contain other pesticides such as resmethrin in addition to chlorpyrifos in their formulations. The products registered for manufacturing purposes are mostly emulsifiable concentrates or dusts containing as high as 99% active ingredient (a.i.). Most ready-to-use home use products contain only 0.5% chlorpyrifos. Products for agricultural uses are mostly emulsifiable concentrates or wettable powders that require dilution. An emulsifiable concentrate of 40.7% a.i., for example, contains 4 pounds (lbs) of chlorpyrifos per gallon.

Label Precautions

The guidance issued by the U.S. EPA for reregistration of chlorpyrifos requires all manufacturing and end use products containing 15% or greater chlorpyrifos to bear the signal word "Warning". Products containing less than 15% chlorpyrifos are classified as toxicity category III with the signal word "Caution". However, there are a number of product labels in DPR files that contain less than 15% chlorpyrifos, bearing the signal word "Warning". The hazards of ingestion, dermal absorption, inhalation, and eye and skin irritation are indicated on the label of chlorpyrifos-containing products. A statement of practical treatment is also included on each label. Chlorpyrifos is a cholinesterase inhibitor. The labels advise atropine by injection as an antidote. The labels also require the handler to wash thoroughly with soap and water after handling and before eating and smoking.

The label reentry interval for treated agricultural areas is 24 hours. The reentry into any citrus orchard treated with chlorpyrifos is two days in California (Title 3, California Administrative Code, Section 6772, 1991). The preharvest interval varies greatly with crops. Protective clothing consisting of a hat, a long-sleeved shirt, long pants , boots, and gloves is required when handling wettable powder chlorpyrifos formulations for agricultural uses. A pesticide respirator jointly approved by Mining Enforcement and Safety Administration (MESA) and National Institute for Occupational Safety and Health (NIOSH) is also required when loading the spray tank or handling a wettable powder formulation for agricultural uses. Protective clothing, rubber gloves, and goggles are required when handling emulsifiable concentrate formulations for agricultural uses. Some chlorpyrifos-containing products that are labeled for use by commercial applicators require protective clothing (long-sleeved shirt, long pants, and shoes), chemical-resistant gloves, and eye protection when handling.

Household and industrial use product labels prohibit users from allowing children or pets to contact treated surfaces until spray has dried. The labels also prohibit using chlorpyrifos on edible products, in areas of food processing plants, in restaurants or other areas where food is commercially prepared or processed, or where food is exposed.

The users of products for structural pest control and turf are directed by the label statements to wear a face shield or goggles, neoprene or natural rubber gloves, foot wear, a long-sleeved shirt, and long pants or coveralls when handling. A mask or respirator is required when using the product in confined areas.

It must be kept in mind that the statements of protective measures (clothing and equipment) on the labels on file are inconsistent, or appear only on certain labels. The U.S. EPA guidance for the reregistration of pesticide products containing chlorpyrifos does not specify any protective clothing or equipment for persons handling these products.

USAGE

Chlorpyrifos has a wide range of agricultural and non-agricultural uses for control of a variety of foliar, soil, and household pests. As of June 1993, there are 420 chlorpyrifos-containing products registered in California. Approximately half of these products are labeled for industrial or household indoor (including pets) and/or outdoor uses. Other uses include agricultural, domestic animals, turf areas, home garden, and structural pest control (Pesticide Registration Branch, 1993). Reports of pesticide use indicate that approximately 2,097,264 lbs of chlorpyrifos were used in California in 1991 (DPR, 1991a). About 47% of the reported use (995,723 lbs) was on alfalfa, almonds, cole crops, cotton, oranges, and sugar beets with over 800,000 acres treated. Structural pest control reported use was 693,354 lbs for the same year. The report of pesticide sold indicates a total of approximately 2,412,629 lbs of chlorpyrifos sold in California in 1991 (DPR, 1991b).

The rate of application for agricultural uses varies with the crop. Chlorpyrifos can be used for agricultural purposes as foliar treatment, soil incorporation, seed treatment, dip, through irrigation, and by air. In non-agricultural areas, it can be applied as a surface spray, trench, crack and crevice, injection, fogger, bait, or impregnated material.

WORKER ILLNESS/INJURY

From the period 1982-1989 there were 365 illnesses reported where chlorpyrifos was the sole pesticide judged to be the cause of the illness (Chl-A) and 302 where illnesses were caused by chlorpyrifos in combination (Chl-C) with other pesticides (Edmiston, 1991). With respect to the type of symptoms for these groups there were 74% and 84%, respectively, systemic illnesses for the chlorpyrifos alone (Chl-A) and chlorpyrifos in combination (Chl-C). As to the types of the illnesses, 85.2% of Chl-A and and 83.8% of Chl-C occurred as a result of a non-agricultural application of chlorpyrifos. These data reflect the significant structural uses of this insecticide alone or in combination. The work activity most commonly involved when the exposure occurred was classified as Nonocc B (including exposure following structural applications, exposure to drift from agricultural applications, cleaning/repairing equipment) with 35.6% for Chl-A and 55.7% for Chl-C. These illness data are illustrated in Figures 1-4. The data in these figures list the number of cases for each category.

Data obtained from the Pesticide Illness Surveillance Program (PISP) in California indicate that there are numerous illnesses associated with structural applications of organophosphorus insecticides (OPIs). Of particular concern are the illnesses reported by office workers and homeowners who become ill after entering a treated area. *A priori,* it is not possible to determine whether the illnesses are caused by (a) the active ingredient, (b) formulation constituents or (c) manufacturing impurities. Analysis of literature data on the active ingredient residue levels (air and surfaces) 2-4 hours after application coupled with acute toxicity information indicates that there are insufficient pesticide residues to cause a cholinesterase-related illness. A similar type of analysis of the formulation ingredients (Vaccaro, 1990) and their likely environmental levels suggest that it is unlikely that these are the cause of the illnesses. Since neither the active ingredient nor the formulation constituents are a likely cause of the OPI illnesses, other possible agents for the non-specific symptoms that are reported have been considered. Literature information and an understanding of manufacture and reactions of OPIs suggest that volatile mercaptan impurities (mercaptans, thioethers, disulfides and trisulfides) present in chlorpyrifos (Vaccaro, 1990) are the likely cause of the illnesses. The physiological symptoms (nausea, headache, eye effects and in some cases diarrhea) resultant from exposure to these volatile, malodorous organics (NIOSH, 1978) are similar to those reported by humans after exposure to organophosphorus insecticides after structural applications (Sanborn *et al.*, 1992).

DERMAL TOXICITY AND EYE IRRITATION

Dermal toxicity and sensitization

Dermal toxicity of chlopyrifos ranges from moderate to low. The dermal LD_{50} of undiluted technical chlorpyrifos moistened with saline solution in rabbits is >2,000 mg/kg of body weight (Burns, 1981). The dermal LD_{50} in rabbits (mixed sex) for chlorpyrifos in formulated products ranged from 1,180 to 6,730 mg/kg of body weight (Burns, 1981). Dursban® was tested on these two groups using different formulations. The 2E and 4E formulations had LD_{50}'s in female rabbits of 620 and 530 mg/kg, respectively. The mixed-sex test group had values of 4,000 and 1,185 mg/kg. This pattern held for three other formulations tested, except for the "Dursban® Household Insecticide" formulation, where the female exhibited greater tolerance (12,930 mg/kg) than the mixed-sex group (6,730 mg/kg). Two additional formulations were taken to their highest doses without establishing LD_{50}'s.

Potential dermal sensitization of Dursban® 6 insecticide containing 62.5% chlorpyrifos (for manufacturing use only) was evaluated using male Hartley albino guinea pigs (Carreon, 1985). The undiluted dose of 0.1 mL Dursban® 6 was applied to a 15mm x 15mm gauze square patch, placed on the clipped area of the back, secured and covered with adhesive tape. Four applications were made within 10 days. Dermal sensitization potential of this chemical was compared with a positive control using DER 331 epoxy resin prepared as a 10% solution in Dowanol® DPM/Tween 80 (9:1). After a minimum of 2 weeks the animals were challenged with undiluted Dursban® 6 and DER 331 epoxy resin. The results indicated Dursban® 6 insecticide was a (mild) skin sensitizer. The same result was also observed with to other products, Dursban® 6R and Dursban® HF Insecticidal Concentrate, both of which are for manufacturing only.

Potential dermal sensitization of Dursban® Microencapsulated (ME) Insecticide containing 12.32% chlorpyrifos was also evaluated using male Hartley albino guinea pigs (Carreon, 1986). A similar procedure used for chlorpyrifos insecticidal concentrate was employed. The results indicated Dursban® ME insecticide was not a potential human skin sensitizer. Similar results were observed with XRM-4656 chlorpyrifos formulation containing 22.95% a.i. (Jeffrey, 1986).

Dermal and eye irritation

Dursban® fogger formulation containing chlorpyrifos (0.05% a.i.) and d-trans allethrin (0.05% a.i.) were tested in rabbits for potential skin and eye irritation (Kukulinski, 1983). This product was shown to cause some skin irritation (moderate to severe erythema and edema) and was classified as Toxicity Category III (Caution). This product also produced

some eye irritation and was classified as Toxicity Category III (Caution). "ProTurf Fertilizer Plus Insecticide III" containing 92.59% fertilizer and 0.98% chlorpyrifos did not cause any eye and skin irritation in young adult rabbits (Ferguson, 1977).
Examples of products tested that were shown to cause temporary eye and skin irritation are: Killmaster II containing 2% a.i. (Conine, 1983), and XRM-4656 containing 22.95% a.i. (Carreon, *et al*., 1982). Overall, chlorpyrifos or chlorpyrifos products may cause temporary skin or eye irritation; chlorpyrifos products were classified as category II or III.

DERMAL ABSORPTION

Goat

Goats were used to investigate dermal absorption rates in animals (Cheng *et al.*, 1989). Two male goats, weighing 15 and 18 kg, were dermally treated with 22 mg/kg of ^{14}C-chlorpyrifos (from Dursban® 44). The treated area, on the right shoulder, was prepared by shaving an 8 x 10 inch square and attaching a four-inch diameter ring to the center. One mL of the test solution was applied to the skin (achieving the 22 mg/kg dose) and spread with a glass rod. The carrier solvent was not specified. The tested area was occluded with a filter paper cap. Maximum absorption as specified by the blood radioactivity levels, was at 12 hours post-exposure and was estimated as 0.3 percent in 12 hours, based on a blood chlorpyrifos level of 0.836 ppm. Mass-balance recovery was not given. It appears that the major thrust of this study was metabolic distribution of the urinary metabolite (3,5,6-trichloropyridinol) and chlorpyrifos.

Human

A dermal and oral absorption study was conducted in six healthy volunteers (Nolan *et al*., 1982). Six human subjects (mean weight = 83.3$\pm$10.3 kg) were first given a 0.5 mg/kg oral dosage, via 0.5 gm lactose tablet, of chlorpyrifos (99.9% purity). Both blood (erythrocyte and plasma cholinesterase activity, chlorpyrifos and metabolites) and urine (chlorpyrifos and metabolites) samples were collected. Two weeks later the same subjects were exposed via the dermal route. One volunteer (weight = 77.1 kg) was exposed to 0.5 mg/kg (~0.39 mg/cm^2) and five volunteers were exposed to 5.0 mg/kg (~4.2 mg/cm^2) of chlorpyrifos dissolved in dipropylene glycol methyl ether (DPGME). There was no attempt to occlude the forearm application site (~100 cm^2) nor were the subjects required to alter their bathing. The wash-off time (either a tub bath or a shower) was 12 to 20 hours post-application. Dermal doses used in this study were too high compared to recommended doses (Zendzian, 1989) and the expected occupational exposure. Therefore, dermal absorption was estimated at the dermal dose of 10 ug/cm^2 by extrapolation of the available data (Thongsinthusak and Krieger, 1991). A dermal dose of 10 ug/cm^2 is in a normal range for a dermal absorption study and occupational exposure. Doses in log scale were plotted versus the corresponding percent administered doses excreted in urine. A straight line with a coefficient of determination (R^2) of 0.85 was obtained. Dermal absorption was estimated from a dermal dose of 10 ug/cm^2. The dermal absorption value was corrected for incomplete accountability from dermal route according to a principle reported by Feldmann and Maibach (1974) or Wester and Maibach (1985). Dermal absorption of 9.6 percent was estimated and used in the calculation of worker exposure estimates. This dermal absorption value was similar to that previously determined by Knaak (1982) where a different approach was used in the estimation. Knaak estimated 9.3% of a dermal dose would be absorbed over a 20-hour period.

ANIMAL METABOLISM

Metabolism studies of chlorpyrifos were performed to determine the fate, metabolic products and excretion kinetics. Metabolism studies were done in humans and in animals, including rats, goats, and sheep.

Humans

Healthy human volunteers were administered a single oral or dermal dose of chlorpyrifos in the pharmacokinetic study (Nolan *et al.*, 1982). Following a single oral dose of chlorpyrifos (99.8%) at 0.5 mg/kg (n=6), 70±11% of the administered dose was recovered in urine as 3,5,6-trichloro-2-pyridinol (3,5,6-TCP), a principal chlorpyrifos metabolite, and probably 3,5,6-TCP glucuronide. Absorption and elimination half-lives were 0.5 hour and 26.9 hours, respectively. Peak 3,5,6-TCP excretion was reached in about 6 hours after administration. Plasma cholinesterase was depressed to 15±1% of the pre-dose level and it recovered to a normal level in about 30 days.

Following a single dermal dose at 0.5 mg/kg (~0.39 mg/cm^2, n=1), 2.6% of the dose was recovered in urine (Nolan *et al.*, 1982). For a dermal dose of 5.0 mg/kg (or ~4.2 mg/cm^2, n=5), 1.02±0.6% of the dose was recovered in urine as 3,5,6-TCP. Excretion peaked at about 2 days and leveled off slowly from 2 to 7 days after the exposure. Plasma cholinesterase decreased about 13%. No signs or symptoms of toxicity were observed in any of the volunteers who received oral or dermal doses. No unchanged chlorpyrifos was found in the urine. Also, changes were not observed in erythrocyte cholinesterase activity at any dose. Based on absorption and excretion kinetics, chlorpyrifos and 3,5,6-TCP have low potential to accumulate in man.

Rats

The rat (CDF Fischer 344) study (Nolan *et al.*, 1987) used ^{14}C-ring labeled chlorpyrifos in corn oil administered by gavage. There were three dosing regimes; 1 dose of 0.5 mg/kg, 1 dose of 25 mg/kg; 15 daily doses of 0.5 mg/kg of unlabeled chlorpyrifos then 1 dose of 0.5 mg/kg of ^{14}C-chlorpyrifos. There were five rats per sex per dosing group. The rats were sacrificed either three days (males) or six days (females) after the last dose. All tissues, urine, feces and respired air were sampled. Recovery of ^{14}C averaged 97.5 percent.

The predominate route of excretion was urinary which ranged from 83.9 to 91.7 percent. The average urine value was 88 percent (males-88.6%, females-87.5%). The metabolite excreted was either 3,5,6-TCP, 3,5,6-TCP glucuronide or tentatively 3,5,6-TCP sulfate. Fecal excretion ranged from 5.5 to 11.5 percent, averaging 8 percent. The cage wash averaged one percent and the carcass retained less than 0.5 percent. Air monitoring showed only trace amounts. No unmetabolized chlorpyrifos was recovered in urine. The half-lives for chlorpyrifos were dose, frequency and sex dependent. The one dose at 0.5 mg/kg had a half-life of 8-9 hours for both sexes; the one dose at 25 mg/kg and the multiple 0.5 mg/kg both had half-lives of 12.4 hours for the males and 23.2 hours for the females.

Goats

Two goat studies were reviewed (Cheng *et al*., 1989; Glass, 1981). The previously cited (DERMAL ABSORPTION) goat study (Cheng *et al*., 1989) investigated the metabolic fate of ^{14}C-chlorpyrifos in blank Dursban® 44 formulation after dermal exposure. The dose rate was 22 mg/kg administered (approximately one mL of the solution) onto the shaved shoulder (4-in. diameter) of two male goats. Animals were sacrified approximately 18 hours after exposure. The tissues sampled were liver, kidney, heart, omental fat and muscle. The mean chlorpyrifos equivalents (ppm) recovered were: liver 0.48, kidney 0.59, heart 0.37, omental fat 0.62, and skeletal muscle 0.07. Further extraction to characterize the metabolite profiles in the tissues of animal number one which contained the highest radioactivity was performed. The two major constituents identified were chlorpyrifos (primarily in the heart and omental fat) and the metabolite 3,5,6-TCP (in the liver and kidney). Muscles contained roughly equal amounts of the two materials.

The second study (Glass, 1981) used two lactating goats dosed by the oral route. The doses were prepared in gelatin capsules. The dosages were equivalent to 16 and 25 ppm in the feed. The animals were fed the doses twice daily for 10 days and sacrified on the 11th day. Urine, feces, milk and tissues were collected for analysis. The orally administered dose was rapidly excreted in urine. The majority of the radioactivity (80.3%) was discovered in urine with smaller amounts in feces (3.6%), gut (0.9%), tissue (0.8%), and milk (0.1%). Total recovery of administered doses averaged 85.6 percent.

Most metabolic products excreted in urine were the beta-glucuronide of 3,5,6-TCP with smaller amounts of 3,5,6-TCP and a minor amount identified as S-ethyl-(3,5,6-trichloro-2-pyridyl) phosphorothioic acid. The tissues/organs with the greatest average amount of ^{14}C residue after 10 days were the rumen (0.44 ppm), the lower gut (0.39 ppm), the ovaries (0.32 ppm), the blood (0.30 ppm), and the kidney (0.25 ppm). All other tissues/organs had 0.20 ppm or less, with bone, muscle and brain having 0.02 or less. Three tissues underwent chemical identity analysis of the ^{14}C activity: fat, liver and kidney. In fat, the parent material accounted for 76.5 percent of the radiolabeled material, the remaining extractable 21 percent was identified as metabolite, primarily 3,5,6-TCP. In both liver and kidney, the reverse was true, with 83.5 (liver), to 92 (kidney) percent of the radiolabel identified as 3,5,6-TCP and minor percentages (maximum 3.5) appearing as parent material. The half-life of chlorpyrifos, based on urine recovery relative to applied dose, was 6 days in one goat, seven days in the other.

Sheep

Sheep have also been treated with formulated material (Dursban® 44: 43.2 percent a.i.) and studied for residue distribution (Dishburger, 1979). Dursban ®44 was applied at a rate of 1 mL formulation/50 lbs (0.044 mL/kg). The material was applied to a 4 to 6 square inches shorn area of the back of the animals. There were 22 female sheep in the test group: 19 treated and 3 controls. Three animals were sacrificed weekly for 5 weeks, whereas, four animals were slaughtered at 6 weeks post-treatment. Samples were collected of fat, muscle, liver, and kidney and analyzed for chlorpyrifos and 3,5,6-TCP. As shown ealier in the goat study, the distribution of chlorpyrifos and 3,5,6-TCP was tissue dependent. Fat residues were overwhelmingly chlorpyrifos while liver, kidney and muscle contained either 3,5,6-TCP (kidney, liver) or negligible amounts of both (muscle). TCP was not found in fat samples three weeks post-treatment. By six weeks, muscle, liver and kidney were essentially free of residues while the omental fat still had up to 0.042 ppm chlorpyrifos.

EXPOSURE ASSESSMENT

Exposure data for chlorpyrifos were limited to only a few agricultural and residential uses. Occupational exposure studies of other pesticides with similar use patterns were utilized to estimate exposure for growers, pest control operators and home gardeners. The degree of exposure was assumed to be proportional to the amount of a.i. handled. The data from these surrogate studies were adjusted to reflect the application rates permitted by the chlorpyrifos label for the same use. Exposure monitoring studies for mixer/loaders, applicators (Honeycutt, 1992a) and harvesters (Honeycutt, 1992b) are currently being conducted in citrus.

A. <u>Residential Uses</u>

Approximately 33% of the chlorpyrifos in California was utilized by structural pest control operators for the control of termites and wood destroying insects (DPR, 1991a). Chlorpyrifos products registered solely for use by pest control operators, are formulated with a maximum of 4 lbs of a.i. per gallon. These products are applied as a 1.0% mixture with water to control termites in the foundations of buildings. Products registered for use by home gardeners to control termites are formulated with a maximum of 12.6% a.i. Their labels permit applications as a 0.5% mixture to infested soil around foundations and fence posts.

A.1 Structural Pest Control Operators (Termite control)

The dermal and inhalation exposure to Dursban® T.C. (Dow Chemical, 4 lbs a.i./gal) was observed for eight structural pest control operators in New Jersey (Fenske and Elkner, 1990). Chlorpyrifos was mixed as a 1% solution (two gallons of product in 98 gallons of water) and applied by sub-slab and soil injection to the foundations, three of which had crawl spaces. The workers, working in pairs to treat four structures, were monitored while performing three full workdays and one partial workday. Dermal exposure was detected with handwashes and gauze patches attached to various locations of the body. Patches were placed outside the workers clothing at the neck, chest and both shoulders to measure exposure to the head and neck regions and underneath the worker's clothing at the forearms, and upper and lower legs to detect exposure to protected regions. Inhalation exposure was measured with personal air-pumps equipped with glass fiber filters. Urine was collected over a 72-hour period to determine what percentage of the absorbed dose was excreted as metabolites.

The clothing worn by the workers was not standardized and gloves were not worn during most of the application activities. Six of the operators rolled up their sleeves to their elbows, exposing the forearm patches. Only the patch data from the three full workdays were used in the analysis for the exposure assessment. Standard U.S. EPA methods for calculating dermal exposure were used to estimate the exposure to the workers (U.S. EPA, 1987).

The operators, working an average of 6.9 hours per day, took approximately 2.8 hours of that time to make one application of 9.9 lbs (mean) of chlorpyrifos. The remaining 4.1 hours were spent preparing the site (Fenske and Elkner, 1990) for treatment. The workers experienced 5.9 mg/hour (range 1.7-11.1 mg) of dermal exposure during the application time with a total of 16.5 mg (range 4.8-31.1) of exposure during one workday. Travel time to and from the job site was not included. The upper and lower legs contributed 51% of the exposure while the forearms accounted for 33.8% of the exposure. Exposure to the hands accounted for only 7.2%. The squatting and crawling that workers do when treating foundations with crawl spaces may account for this distribution of the dermal exposure. Although the dermal exposure was not quantified for the torso body regions (chest, stomach and back), it can be estimated with U.S. EPA standard methods. Using the results from the chest and back patches in conjunction with the appropriate body surface areas, the estimated potential dermal exposure is 0.89 mg/hour. Assuming the work clothing worn by the operators provided 89% protection from exposure, the calculated dermal exposure from these body regions represents less than 2% of the observed dermal dose per hour. The chlorpyrifos air concentrations averaged 26.5 ug/m^3 during the 2.8 hour application period. Using a tidal volume of 29 L/minute (U.S. EPA, 1987), the inhalation exposure was estimated at 0.13 mg for the application period.

Results from the bio-monitoring phase of the study indicate that all workers had been exposed previously to chlorpyrifos and were still excreting the metabolites in their urine when the study started (Fenske and Elkner, 1990). Seventy-two hours after the study started, metabolites were still being excreted at 45% of the maximum rate observed at 18-24 hours. This indicates the complete excretion of chlorpyrifos metabolites in urine requires more than three days. The bio-monitoring data from this study cannot be used to quantify the absorbed dose of chlorpyrifos for structural pest control operators exposed to Dursban® T. C.

The application of termite control pesticides under California conditions was characterized in a report by Brodberg (1990). In California most termite control applications are made to structures with concrete slab or crawl space foundations. The report noted that treating structures with crawl space foundations incurred some of the greatest exposures for structural pest control operators. The report also observed that application activities (mixing/loading, applying and patching the injection holes) involve about 40% of the work time with the remaining time spent driving to the site, surveying the structure and drilling the injection holes. Depending on the floor plan and size of the structure, one to two pest control operators can treat one foundation during an eight hour workday.

A.2 Residential Pest Control Operators

Some chlorpyrifos products with greater concentrations than 12.6% of active ingredient such as Dursban 50W (50% a.i.) are registered for use by commercial applicators only. These products are used to control pests in turf and landscapes. The application rate is 0.34 oz per 1,000 ft^2 or one pound a.i. per acre. Commercial applicators can make applications to 12 locations per day and may work on an average of 223 days (range 185-250 days) per year (Munro, 1992). Exposure estimates were obtained from the application of Dursban® 50W by three commercial applicators (Gibbons *et al.*, 1993). These workers wore protective clothing as required on the product label which included long-sleeved shirts and pants or coveralls, eye protection, chemical-resistant gloves and boots. These applicators applied chlorpyrifos in an eight-hour workday for 5 or 6 days.

For biological monitoring, urine samples were collected daily until the end of the application period. Urinary 3,5,6-TCP as well as creatinine were analyzed and used to estimate the absorbed daily dosage for chlorpyrifos. From a pharmacokinetic study by Nolan *et al.* (1982), the maximum excretion of 3,5,6-TCP was attained 1.2 to 2 days after dermal administration of chlorpyrifos to human volunteers. Therefore, urinary TCP from day 2 to day 5 or day 6, depending on the application period, was used. Urinary creatinine level was used as a means to normalize the incomplete urinary collection for certain periods.

Estimation of absorbed daily dosage (ADD) of chlorpyrifos from urinary 3,5,6-TCP was based on the pharmacokinetic study conducted by Nolan *et al.* (1982) where 70% of the oral dose of radiolabeled chlorpyrifos was excreted in urine as 3,5,6-TCP. Absorbed daily dosage of chlorpyrifos for the commercial applicators was then estimated using the relationship of the urinary excretion of 3,5,6-TCP after oral administration (3,5,6-TCP (ug) found in urine ÷ 0.70). The absorbed dosage is subsequently corrected for the difference in molecular weight of chlorpyrifos and 3,5,6-TCP (ADD x 351 ÷ 198.5). The geometric mean for ADD is 150.8 (±2.8) ug/person/day. The results are shown in Table 1.

A.3 Home Gardeners

Home garden labels of chlorpyrifos are registered for outdoor uses to control insect pests, spiders and ticks in home lawns, ornamental plants and around residential buildings. A surrogate study was used to estimate the dermal exposure incurred when a home gardener applies chlorpyrifos to control infestations of fleas, earwigs and sod webworms in a lawn. The exposure was estimated from an application of an E.C. formulation with 6.8% a.i. by weight at the rate of 12 tablespoons per 1,000 square feet. It was assumed the home gardener took one hour to mix and apply 30 gallons of spray mix with a compressed air sprayer to one thousand square feet of lawn area. The study by Kurtz and Bode (1985) measured the exposure that occurred to home gardeners treating corn and beans with various formulations of carbaryl. To approximate the parameters of the lawn treatment, only data from the applications of the E.C. formulation (Union Carbide XLR-43% a.i.) on beans were used. The subjects took 15 minutes to mix and apply a mixture of one tablespoon of product in 0.75 gallons of water. The dermal exposure to various parts of the body was detected with handwashes and gauze pads attached to the coveralls worn by the applicators. Exposure to the face was detected with a mask worn over the nose and mouth. Inhalation exposure was not monitored. The mean values of the results from the 12 replicates were used to estimate the dermal exposure to the home gardener.

The subjects applied three grams of a.i. during a 15 minute period and experienced a potential whole body exposure of 6.8 mg. This is equivalent to 2.27 mg of potential dermal exposure per gram a.i. applied. Of this, 47.6 ug or 0.7% of the total potential dermal exposure occurred to the hands. To extrapolate this quantified value to the theoretical exposure for the chlorpyrifos treatment, a conversion factor of 2.27 mg of potential dermal exposure per gram a.i. handled was used. Assuming the home gardener took one hour to treat the lawn and applied 30 gallons of spray mix, this would entail handling six ounces of product containing 0.023 lb a.i.. With the conversion factor, this would be the equivalent of handling 10.4 gm of a.i. and experiencing 23.6 mg of potential dermal exposure per day.

Inhalation exposure was not monitored directly, but estimated by comparing the exposure on the dust mask to that detected on the adjacent pads. The exposure detected on the shoulder pads was subtracted from an equivalent expression of exposure based on a 25 cm^2 surface area for the mask. A mean value of 3.5 ug of inhalation exposure was estimated from applying three gm a.i. on the beans. If the gardener applied a total of 10.4 gm a.i. during one hour of spraying, the inhalation exposure would be 12.1 ug (10.4 gm x 3.5 ug ÷ 3 gm).

A.4 Crack and crevice applications

Exposure estimates for chlorpyrifos were not available for pest control operators during the application to cracks and crevices. Surrogate exposure estimates were obtained from the application of three formulations of propoxur to houses in 12 locations in a workday (Sanborn, 1993). Propoxur formulations used in this study were 0.95% finished product and 1.1% spray mixes prepared from 70WP formulation. These two formulations represent the application of chlorpyrifos residual Crack and Crevice® injection system (e.g. PT® 270 Dursban®) and Dursban® L. O. or Dursban® ME. The last two products are used to control numerous pests in and around households.

Three applicators who applied propoxur wore denim trousers, 35/65% cotton/polyester long-sleeved shirts and leather boots/shoes or cloth sneakers. In addition to or in place of their work clothing, cotton coveralls, baseball caps, and nitrile gloves were worn by the applicators. This clothing protection is similar to that required for chlorpyrifos application. Dermal exposure was estimated from patch dosimeters placed under the clothing and ethanol hand washes. Inhalation exposure was obtained by using a personal air pump set at a flow rate of 1 L/min. Dermal and inhalation exposures are corrected to reflect the maximum application rate of 0.5% for chlorpyrifos. Results presented as geometric means are shown in Table 1.

B. **Agricultural Uses**

Chlorpyrifos is registered for use on most ornamental and agricultural crops with the major use occurring on alfalfa, cotton, citrus, walnut, and sugar beets. The label rates range from 0.5-3.0 lbs of a.i. per acre for most field crops to a maximum of 6 lbs a.i. per acre for citrus. The occupational exposure was estimated for workers mixing/loading and applying chlorpyrifos with aircraft, air-blast orchard sprayers and fixed-boom ground rigs, by hand boom in greenhouses and for pilots and flaggers.

B.1 Orchard Applicator

In 1985, the Agricultural Products Department of Dow Chemical conducted a study monitoring the exposure to operators from applying Lorsban® 50 WP in orchards (Bohl *et al.*, 1985). Five different operators were monitored with dermal dosimetry and air sampling to estimate exposure and blood sampling to detect cholinesterase inhibition. Urine samples were collected before and for 72-79 hours after the start of the chlorpyrifos application. The amount of chlorpyrifos absorbed into the body was calculated by observing the rate of metabolite excretion in the urine.

However, problems with the results of this study preclude its use in estimating the occupational exposure to chlorpyrifos. The value of the bio-monitoring data is limited due to the intervals at which the urine samples were saved and the abbreviated period the samples were collected. When the excretion data was plotted on standard graph paper, the accumulative excretion curve for each of the applicators, had not reached a plateau after 72-79 hours, indicating additional excretion would occur. The steepness of the curve infers that total excretion of the major metabolite would not occur during the collection period. Only one applicator collected the urine specimens at intervals that allowed the excretion pattern to be characterized. The excretion data from the other workers is not adequate for use in the pharmacokinetic model described by Nolan *et al.*(1982) to estimate the absorbed amount of chlorpyrifos.

Exposure to the hands was monitored for only one of the five applicators. For this one applicator, the exposure to the hands accounted for approximately 74.5% of the dermal exposure for the whole body. The omission of the hand exposure component in the study may have resulted in a gross underestimation of the dermal exposure for the other four applicators. Although an additional worker exposure study is now in progress for the application of chlorpyrifos in citrus (Honeycutt, 1992a, b), the results are not yet available.

To estimate the potential exposure from applying chlorpyrifos in a citrus grove at the maximum label rate, a surrogate amitraz study was used. An applicator exposure study was conducted for Mitac® WP (amitraz) applied in pear orchards located in the state of Washington (Haskell, 1990). Six different operators mixed, loaded and applied amitraz with air-blast orchard sprayers at the rate of 1.5 lbs a.i. per acre with 400 gallons of water. Exposure was detected with dermal dosimetry (gauze patches), handwashes, micro air pumps and urine testing. The gauze patches and air sampling cartridges with glass fiber filters were changed at lunch time and as necessary during the mixing/loading and application to prevent saturation. Handwashes were performed at lunch time and at the end of the day in Ziploc® bags filled with 0.5-1.0% Sur-Ten® solution and water. Urine was collected before application and post-application in pooled 24 and 48 hour samples.

The study protocol was well designed and the results from the field study were presented in detail. The six operators mixed, loaded and sprayed 13 to 17 loads each per day, applying 19.5 to 25.5 lbs a.i. The mean mixing/loading time was six minutes and the mean application time was 22 minutes per load. The operators averaged 6.7 hours of handling time per day. The potential dermal exposure, excluding the hands, averaged 510 mg per operator for a 6.7 hour work period. Since the label requires mixer/loaders and applicators to wear rubber gloves, exposure to the hands was minimal with a mean value of 3.2 mg. The mean inhalation exposure was 0.61 mg for the six operators.

To extrapolate the potential exposure from treating a citrus grove with chlorpyrifos, some conversions were necessary. The observed potential dermal and inhalation exposures were increased 4 fold to account for the maximum citrus label rate of 6 lbs of a.i. per acre. The 6.7 hour work period was equivalent to an 8 hour workday because of the extra time needed to mix and load material for a 6 lbs a.i. per acre treatment and to account for travel time to and from the application site.

B.2 Greenhouse Applicators

Chlorpyrifos is registered for use in controlling insect pests in turf and ornamental crops grown in greenhouses. A study by Stamper *et al*. (1989) was used to estimate the occupational exposure from a greenhouse application. The dermal and inhalation exposures from applying chlorpyrifos and three other pesticides were monitored in two greenhouses located in Florida. Two male and two female subjects made several chlorpyrifos applications each to growing chrysanthemums and African violets. The applications were made with a hand-held wand equipped with six nozzles and attached to a centrally located mix tank by a long hose. All the applicators wore a minimum of coveralls (Tyvek®), hood, rubber gloves, boots and respirator during every application. In addition, some applications were made wearing goggles and an apron.

Potential dermal exposure was detected with patches constructed of alpha-cellulose with a glassine weighing paper backing. These dermal dosimeters were attached to the outside of the protective clothing at various locations. Patches were also placed underneath the coveralls at the chest, both forearms, thighs and shins to observe the ability of chlorpyrifos to penetrate the protective clothing. The hands of each applicator were washed separately in a plastic bag containing 200 ml of 95% ethanol to measure the actual exposure to the hands. Inhalation exposure was monitored by sampling the concentration of pesticide contamination in the air with the use of a personal air sampler equipped with a polyurethane foam filter plug. Results were reported in relation to the amount of exposure that occurred per hour of spray time or as a mean for all applicators applying the same pesticide. The average spray time for all the applications was approximately one half hour. The percent clothing penetration was estimated by dividing the residues detected in the patch located underneath the protective clothing by the residues present on the corresponding patch located on top of the protective clothing. For the body locations sampled (chest, forearms, thighs and shins), the Tyvek® alone provided a calculated 89% protection.

The mean total body accumulation rate for the three workers making the chlorpyrifos applications was 269 mg/kg of a.i. applied. This expression of exposure approximates the measurement of potential dermal exposure to the body, excluding exposure to the hands. The residues detected in the handwashes of the applicators was 1.6 mg/kg of a.i. applied.

The mean application rate for the three workers was 0.09 kg of a.i. per hour. If the workers sprayed for a maximum of three hours (Rech and Edmiston, 1988), they would apply 0.27 kg of a.i. and experience 72.6 mg of potential dermal exposure and 0.43 mg of dermal exposure to the hands. Using the derived clothing protection factor of 89%, only 11% of the 72.6 mg penetrated the protective clothing to become dermal exposure. This value (8.0 mg) plus the 0.43 mg of exposure to the hands, provided an estimate of 8.43 mg of dermal exposure for an applicator making a greenhouse application of chlorpyrifos. The mean air concentration of chlorpyrifos particulates for the workers was 0.041 ug/L. With an inhalation rate of 29 L/minute (U.S. EPA, 1987), the calculated inhalation exposure after three hours of application was 214 ug.

The application rates in the study need to correlate with the rates permitted by the chlorpyrifos label. Each worker took approximately one half hour to load and apply 0.045 kg of a.i. from a 60 gallon tank equivalent to 0.075 kg per 100 gallons of water. The maximum label rate used to control pests that occur in greenhouses is 0.46 kg of a.i. per 100 gallons of water. To estimate the exposure at this maximum label rate, the values for the dermal exposure to the body, hands, and the inhalation exposure were increased in Table 1 by a factor of 6.1.

B.3 Ground Boom Applicators

The majority of the chlorpyrifos use in field and vegetable crops is to control insect pests in alfalfa, cole crops, sugar beets and cotton. Most of these treatments are made by pest control operators (PCO's) that do custom application work for their customers. Applications to cole crops are often made with tractors equipped with boom sprayers. Much of the application work is done with one worker performing the work tasks of mixing, loading and applying the pesticide. An exposure study that included operators applying an E. C. formulation (Bravo® 500-4.17 lbs a.i./gal) of chlorothalonil with a tractor drawn low-pressure boom sprayer was employed to estimate the occupational exposure to chlorpyrifos from ground sprayer applications (Thongsinthusak *et al*., 1992). The study took place in Florida and involved workers who were experienced in applying pesticides. The chlorothalonil treatments were applied at a rate of 1.43 or 2.22 lbs a.i. per acre to celery and at 2.22 lbs a.i. per acre to tomatoes. Six replications of each treatment were monitored for dermal and inhalation exposure. The workers wore the label required protective clothing (long pants and long-sleeved shirt, goggles and gloves) and it was assumed the goggles did not provide any protection for the face.

Assuming their protective clothing provided 89% protection (Stamper *et al*., 1989) from exposure, the workers mixing, loading and applying chlorothalonil for eight hours with a ground boom sprayer averaged 12.2 mg of dermal exposure per workday. The inhalation exposure averaged 0.20 mg per workday for the same workers. Pesticide use data from the Pesticide Use Report (DPR, 1991a) discloses that a high percentage of the cole crop acreage was treated with chlorpyrifos in 1991. The maximum label rate for this crop is 1.25 lbs a.i. per acre. The mean application rate for chlorothalonil from the 18 replications was 1.96 lbs a.i. per acre. To correct for the difference in application rates, the dermal and inhalation values in Table 1 have been reduced 36%.

B.4 Chemigation Mixer/Loaders

The Lorsban® 4E agriculture use label permits chlorpyrifos to be applied through the sprinkler systems on certain crops. An exposure study was conducted by Kentucky State University to measure the exposure to workers mixing, calibrating and applying chlorpyrifos and insecticides through a center-pivot sprinkler system (Byers *et al*., 1992). Dermal exposure was monitored through the use of gauze patch dosimetry and cotton gloves worn on the hands. Inhalation exposure was measured with a portable air sampler that drew ambient air from the breathing zone at a rate of 2 L/min. The tube was equipped with a polyurethane foam plug to capture the residues for analysis.

The study observed a mean dermal exposure rate of 30.2 mg/hour (range 19.4-44.8 mg/hour) for chlorpyrifos from nine replicates with the worker wearing work clothing. Exposure to the hands accounted for 73% of the total dermal exposure. However, since cotton gloves are known to saturate with active ingredient when used as dosimeters, this value should be interpreted as an eight fold overestimate (Smith *et al*., 1991). The current agriculture-use chlorpyrifos labels require workers handling this pesticide to wear rubber gloves. The exposure rate of 30.2 mg/hour needs to be corrected for the protection provided when rubber gloves are worn by the mixer/loader. Assuming rubber gloves provide 90% protection for the hands (Thongsinthusak *et al*., 1991), the daily dermal exposure is reduced to 10.3 mg/hour or 82.4 mg/day (range 23.0-119.6 mg/day). The mean rate of inhalation exposure observed in the study from the nine replicates was 0.56 mg/day.

The application of chlorpyrifos through chemigation is still an experimental practice in California. Some chemigation applications have been tried with solid set sprinklers to apply Lorsban® in citrus orchards located in the southern coastal valleys (Basabri, 1993) . These applications were made to orchard floors to control infestations of ants that threaten the Integrated Pest Management programs for other citrus pests (Sakovich, 1993). However, questions still linger as to the efficacy of applying chlorpyrifos through this method and the high cost of irrigation water have prevented increased utilization of this method.

B.5 Pilots and Flaggers

Aerial application of chlorpyrifos can incur exposure for the pilots and flaggers directing the application from the ground. A study involving the aerial application of chlorpyrifos on cotton was conducted by the WH&S Branch to estimate the exposure to flaggers from aerial applications (Meinders *et al*., 1991). In this study, a crew of two pilots and six flaggers treated 24,000 acres with 20,000 lbs a.i. over a 28-day period during which urine and dermal dosimetry samples were taken on 12 days. The amount of a.i. applied per day was estimated by assuming the applications took place six days a week with only a half day worked on one of the Saturdays (20,000 ÷ 23.5 = 851 lbs a.i./day). All applications were made at night. Each worker provided urine samples for bio-monitoring and wore cotton T-shirts underneath their work clothing to detect dermal exposure. Detailed observations were made of the actual application times for the pilots and exposure times for the flaggers.

Urine samples were collected from each participant before the applications began and each morning after the night treatments were made. The samples were analyzed for the presence of two diethylphosphate metabolites of chlorpyrifos and for creatinine level. The elimination half-life of chlorpyrifos metabolites is > 3 days such that the urinary metabolites were close to steady state. The creatinine levels were used to estimate what percentage of a 24 hour excretion period the urine sample represented. The cotton T-shirts were worn underneath the work clothing (cotton overalls) during the applications to detect chlorpyrifos residues that penetrated the protective clothing. The assumption was made that the level of residues detected on the T-shirts was representative of the exposure rate for all parts of the body.

A mean ADD of 0.80 ug/kg/day was derived for the six flaggers from the dermal dosimetry. The mean ADD for the pilots was 0.10 ug/kg/day. These exposure rates were derived with a 3% dermal absorption rate divided by the individual body weights. The average work day of the flaggers lasted approximately nine hours with 3.4 hours of actual exposure to chlorpyrifos.

The remaining time was spent waiting for the plane to return from the loading site and driving from one treatment site to the next. The actual exposure time for the pilots was 53% more or 5.2 hours per workday.

This document utilizes a different rate (9.6%) of dermal absorption (Thongsinthusak and Krieger, 1991) to calculate the ADD. To estimate the rate of daily dermal exposure for the flaggers and the pilots shown in Table 1, the ADD's from the study by Meinders *et al*. (1991), were divided by 0.03 (rate of dermal absorption), multiplied by 70 kg (U.S. EPA, 1987) and then divided by 1,000 ug/mg.

The data from the bio-monitoring phase of the study was not utilized for estimating the dermal and inhalation exposure for pilots and flaggers. The T-shirt dosimeters worn by the pilots and flaggers provided an extra layer of protective clothing that mitigated some of the dermal exposure from chlorpyrifos residues penetrating the work clothing. Although text in the study indicated that wearing a T-shirt under their work clothing is a normal practice for pilots and flaggers, a T-shirt is not required to be worn under work clothing by the federal label.

Although inhalation exposure was not monitored, the bio-monitoring data indicate the exposure was minuscule, with many urine samples having levels of the diethylphosphates below the MDL of 50 ppb. This observation that the inhalation route of exposure contributes very little to the total exposure is supported by a review of field exposure studies (Wolfe, 1976). His review surveyed exposure studies for many pesticides to determine which route of exposure (dermal or inhalation) was the most prevalent route of exposure for handlers of pesticides. For most of the studies reviewed, the inhalation component accounted for less than 1 percent of the total exposure. An estimate of the inhalation exposure for pilots and flaggers was derived as one percent of the occupational exposure observed through dermal dosimetry in (Table 1).

B.6 Aerial Mixer/Loaders

Mixer/loaders for aerial applications have the potential to experience some of the greatest exposures to pesticides. They can mix and load enough active ingredient during one workday to treat several hundred acres. A study involving the ground and aerial application of chlorothalonil in Florida was used to estimate the occupational exposure for these pesticide handlers (Thongsinthusak *et al*., 1992). Potential dermal exposure was detected with patches (absorbent paper) attached to the outside of the cotton gloves and work clothing worn by the workers. Inhalation exposure was monitored with a personal air pump that continuously drew air through a micro filter during the work interval. The filtered air was then scrubbed with isopropyl alcohol in an impinger to detect any chlorothalonil vapor residues. Each inhalation sample was a composite of the residues detected by the micro filter and the impinger.

The celery fields were treated with 2.75-4.25 pints (Bravo® 500, 4.17 lbs a.i. per gal) per acre with four gallons of water. Each replicate consisted of the mixer/loader filling a 500 gallon tank with 320 gallons of water and 27.5 or 42.5 gallons of Bravo® 500 and the pilot applying two loads of approximately 160 gallons each. At this dilution rate, the plane could treat 40 acres per load. When the results from the twelve replications of the mixing/loading work tasks were averaged, the workers took 31.5 minutes to mix and load 146 lbs of a.i. In the chlorpyrifos exposure study for pilots and flaggers (Meinders *et al.*, 1991), the actual exposure time (ferrying and spray time at site) for pilots averaged 5.2 hours per workday. This exposure time approximates the actual exposure time per workday for a mixer/loader mixing the spray batches and loading the planes. In 5.2 hours, the mixer/loader could mix and load 10 batches of material handling 1,460 lbs of a.i.

The mean respiratory exposure from the 12 replications was 156 ug/hour or 811 ug from 5.2 hours of exposure per workday. The levels of dermal exposure were reported in ug/in^2/hour. To estimate the dermal exposure for the mixer/loader, the summary of this study as listed in the Appendix B for Chlorothalonil (Thongsinthusak *et al*., 1992) was utilized. The mixer/loaders wore the clothing required by the chlorothalonil label (long pants, long-sleeved shirt, gloves and goggles) with the goggles assumed to provide no protection for the face. The dermal exposure was expressed in mg/person/day and calculated from the potential dermal exposure by utilizing a 10% clothing penetration factor. The values have been normalized to estimate the exposure from working continuously for eight hours per workday. However, since the actual exposure time per workday for the mixer/loader for an aerial application of chlorpyrifos is approximately 5.2 hours, the dermal exposure values in the study were divided by eight and then multiplied by 5.2. The estimated dermal exposure from mixing and loading approximately 1,460 lbs of a.i. per workday was 330 mg/day. To estimate the potential dermal exposure to chlorpyrifos for mixer/loaders, the dermal exposure values for body regions covered by clothing (hands, torso, legs) were increased by a factor of 10 to account for the 10% clothing penetration factor used for chlorothalonil (Thongsinthusak *et al*., 1991). The adjusted estimate for the potential dermal exposure was 3,203 mg/day.

To estimate the occupational exposure to chlorpyrifos for mixer/loaders, the chlorothalonil data has to be adjusted to reflect the Lorsban® label rates and the application techniques used in California. Exclusive applications of chlorpyrifos for a normal workday by an aerial applicator can occur when treating crops like alfalfa, cotton and sugar beets. The maximum label rate for these crops is one lb of a.i. per acre. During peak season use, one mixer/loader can provide enough spray mix for two planes to treat 851 acres (20,000 lbs a.i. ÷ 23.5 days = 851 lbs a.i./day) (Meinders *et al*., 1991). Assuming another worker hauls water for the spray mixing, the mixer/loader could handle 851 lbs of a.i. during a maximum workday. This rate is equivalent to 58% of the 1,460 lbs of chlorothalonil that could be handled during an workday. The dermal and inhalation exposure values for chlorothalonil have been multiplied by 0.58 to adjust for the lower rate of chlorpyrifos applied.

TABLE 1. Occupational Exposure to Chlorpyrifos for Pest Control Operators, Growers and Home Gardeners.

Work Task	Potential Dermal Exposure[a] (mg/person/day)	Daily Exposure[b] (mg/person/day) Dermal[c]	Inhalation[d]	Absorbed Daily Dosage[e] (ug/kg/day)	Seasonal Average Daily Dosage[f] (ug/kg/day)
Apply					
pilot	NA	0.23	0.002	0.33	0.15
flagger	NA	1.90	0.02	2.75	1.24
Mix/Load					
aircraft	1858	209	0.47	290	131
Mix/Load/Apply					
pest control operators					
1. termite control[d]	NA	16.50	0.13	23.60	11.60
2. residential PCO[g]	NA	NA	NA	2.2	1.34 (AADD)*
3. crack and crevice application[g]					
Spray (0.5%)[h]	NA	1.64	0.01	2.30	1.40 (AADD)*
Spray (0.5%)[i]	NA	6.54	0.98	15.97	9.76 (AADD)*
ground boom sprayer	NA	7.81	0.13	11.6	3.7
orchard air-blast sprayer	2040	237	2.44	342	29.50
greenhouse applicator[d]	443	51.40	1.30	79.80	2.60
chemigation	NA	82.4	0.56	117	EA
home gardener	23.6	2.6	0.012	3.7	0.04

Haskell and Thongsinthusak, WH&S, 1993

* AADD was calculated instead of SADD because of year-round uses of chlorpyrifos.
EA Experimental applications only. Use pattern not yet established in California.
NA Not Applicable.

[a] Includes exposure to the hands, except for the orchard air-blast applicator and the greenhouse worker. The workers wore gloves for these two tasks and exposure to the hands was included in the Daily Dermal Exposure.

[b] The Daily Dermal Exposure is derived with the workers wearing the protective clothing required by the chlorpyrifos label for their particular use. The various protective clothing regimes were discussed in the "Label Precautions" section. The requirement for wearing a respirator when handling chlorpyrifos is optional for some product labels. Home gardeners were assumed to be wearing shoes, socks, long pants and long-sleeved shirts.

[c] A penetration factor of 11% (Stamper *et al*., 1989) for coveralls and 10% (Thongsinthusak *et al*., 1991) for chemical-resistant gloves were used to estimate the Daily Dermal Exposure for the whole body including the hands. Eye protection was assumed not to provide any protection for the face.

[d] Exposures for work tasks indicated with a "d" footnote were calculated with workers wearing respirators. NIOSH and/or MSHA approved respirator was assumed to provide 90% protection (Thongsinthusak *et al*., 1991) from inhalation exposure.

[e] The ADD was calculated for a 70-kg man with a dermal absorption rate of 9.6% (Thongsinthusak and Krieger, 1991) or based on biological monitoring for residential PCO. An inhalation uptake of 50% (Raabe, 1988) and absorption rate of 100% were used.

[f] The SADD = ADD x number of application days per season divided by the number of days in use season, except that expressed as AADD for residential PCO and PCOs who do the crack and crevice apllications.

[g] Based on average annual workday of 223 days per year (Munro, 1992). The value represent AADD instead of SADD.

[h] Formulated as 0.5% commercial product.

[i] Prepared as 0.5% chlorpyrifos from commercial formulation prior to application.

Table 2 is used in conjunction with Table 1 to estimate the SADD. This Table lists each work task with the season of use for a particular crop or site and an estimate of the average number of workdays per use season. The sources of these estimates are listed as footnotes after the Table.

Table 2. Season of Use for Crops or Sites with the Maximum Number of Chlorpyrifos Applications.

Work Task	Crop or Site Treated	Use Season	No. of Days Per Use Season	No. of Treatment Days Per Use Season
Apply				
pilot[a]	cotton	July-August	62	28
flagger[a]	cotton	July-August	62	28
Mix/Load				
aerial application[a]	cotton	July-August	62	28
Mix/Load/Apply				
chemigation	oranges	May-September	153	N\A
pest control operators				
1. termite control[b]	structure	year-round	365	180
2. residential PCO[c]	outdoor	year-round	365	223
3. crack and crevice application[c]	indoor	year-round	365	223
ground boom sprayer[d]	cole crop	Mid\May-Mid\Oct.	122	39
orchard air-blast sprayer[e]	oranges	June-November	180	15.5
greenhouse worker[f]	cut flowers	April-September	183	6
home gardener[g]	lawn	year-round	365	4

Haskell, WH&S, 1991

N\A Experimential applications only. Use pattern not yet established in California.

[a] Meinders *et al*. (1991)
[b] Munro (1991)
[c] Munro, 1992
[d] Haskell (1992a)
[e] Horton (1991)
[f] Tsjovold (1991)
[g] Haskell (1991a)

C. <u>Post-Application Worker Exposure</u>

Worker exposure post-application is relatively low for a number of the large scale agricultural uses of chlorpyrifos. Worker exposure in landscape maintenance, sugar beets, corn, alfalfa, almonds, walnuts, pecans, and most cole crops falls in this low exposure group. Classification as low post-application exposure may be the result of the time and target of application (dormant or other spray not targeted to foliage) or low crop contact during cultural practice or harvest. Crops that have the potential for chlorpyrifos exposure to farm workers include Brussels sprouts, fruit trees (various citrus and *Prunus* species), and cotton. Studies observing worker exposure to chlorpyrifos during the harvesting of tree fruits, topping, leaf stripping, and harvesting of Brussels sprouts, and during cotton scouting are not available. Consequently, transfer factors from surrogate studies for similar work activities combined with a DFR value for the chlorpyrifos residues at the time of exposure were used to estimate dermal exposure.

C.1 Topping Brussels sprouts

Post-application worker exposure in Brussels sprouts is expected to be the highest exposure for cole crops because up to 6 applications can be made in a season. Other cole crops are limited to a single application at the same rate. Dislodgeable foliar residue (DFR) data are not available for chlorpyrifos on Brussels sprouts or other cole crops. However, the maximum label rate of 1.0 lb a.i. per acre for Brussels sprouts is the same rate for cotton. Assuming these equivalent application rates yield similar residues, cotton residue data was used to estimate Brussels sprouts residues. The highest DFR residues found on field grown cotton were 1.8 ug/cm^2 (both sides of the leaf surface areas) (Buck *et al*., 1980; Ware *et al*., 1983) at the 1.0 lb a.i./acre rate zero hours after application. A study by Veierov *et al.* (1988) observed the effects of concentration and method application of chlorpyrifos on the deposition of foliar residues and their rates of decay. Greenhouse tomatoes, outdoor potted cotton plants and the foliage of commercial orange trees were treated at various rates (0.02-12.5% tank concentrations) with a low or high volume water application. At the 0.5% rate (1.0 lb a.i./60 gallons of water), the half-life of chlorpyrifos ranged from approximately one day on potted cotton foliage to one-two days on orange foliage. These half-lifes for citrus are supported by results from a previous residue study conducted by Iwata *et al.* (1983) at theUniversity of California Citrus Research Center in Riverside. Although the trees were treated at higher rates (5-10 lbs a.i./acre) with a summer oil (28 gal/acre of NR-440 spray oil), the half-lifes ranged from 2.4-2.8 days on oranges.

Chlorpyrifos applications to Brussels sprouts average four per season although up to six are allowed by the label. Fewer applications are used because during approximately the last 40 days of the season other pesticides are more effective in controlling the changing pest pressure. The first chlorpyrifos application is to seedling plants with minimal foliage. Additional applications are usually made following irrigation, at about 21-day intervals. Assuming a half-life of two days for chlorpyrifos (Veierov *et al*., 1988), less than 1% of the initial residues are still present at the time of the next application. Thus each application can be treated independently when calculating worker exposure. Non-applicator worker exposure occurs during topping (about 40 days pre-harvest when the apical meristem is cut off), during leaf stripping (about 2 days pre-harvest when leaves are removed to completely expose the sprouts), and at harvest.

The cultural practice of topping consists of removing the terminal buds on the plant by hand. Small crews of 5-6 workers walk the rows breaking off the buds in order to stop stem elongation. The plants are 2.5-3 feet tall and the rows are filled in with foliage. Since this practice takes place in July-August, the fields are wet most of the day from the persistent fog that forms this time of year. As a consequence, workers wear rubber rain suits over their work clothing to keep dry although they may or may not wear gloves (Banadelli, 1993). Topping is usually done after the final chlorpyrifos application of the season has been completed. However, the earliest time at which topping could be done would be 12 hours (based on federal farm worker re-entry interval) after the final chlorpyrifos application. DFR residues at this time would be 80.6% of the initial residues of 1.8 ug/cm^2 immediately after application. Residues during leaf stripping and harvest activities will be lower than this. Consequently, topping is expected to be the highest post-application exposure activity for cole crops.

Surrogate exposure studies from similar work activities can provide a transfer factor for use in conjunction with the chlorpyrifos DFR to estimate dermal exposure. The exposure study by Rech *et al*. (1989) of farm workers harvesting pole tomatoes treated with chlorothalonil can simulate the extensive contact with treated foliage that takes place during topping. The study quantified the dermal exposure that occurs to the various parts of the body and measured the ability of chlorothalonil to penetrate the work clothing worn by the harvesters. For workers wearing long pants and long-sleeved shirts or sweaters and no gloves, the observed dermal exposure was 2,670 ug/hour (mean) with the exposure to the arms and torso representing approximately 30% of the total. The study observed a mean clothing penetration rate of 29.6% for chlorothalonil. The potential dermal exposure before clothing penetration can be estimated as 4,575 ug/hour (2,670 ug/hour x 0.30 ÷ 0.296) + (2,670 x 0.70). The exposure to the hands represented 42% of the total potential dermal exposure to the body. This value will be useful in calculating the dermal exposure to the Brussels sprouts workers when rubber rain suits are worn with no gloves.

A transfer factor for estimating the potential dermal exposure for workers harvesting pole tomatoes can be derived by dividing 4,575 ug/hour by the DFR 1.9 ug/cm^2 (both sides of leaf). This value of 2,408 cm^2/hour can be used to estimate the potential dermal exposure for the Brussels sprouts toppers. Assuming the workers top chlorpyrifos treated Brussel sprouts for eight hours per day, the potential dermal exposure would be 27.9 mg/day (1.45 ug/cm^2 x 2,408 cm^2/hour x 8 hours). Farm workers involved in topping work generally wear shoes, long pants, long-sleeved shirt and a hat. This work clothing can be assumed to provide 89% protection (Stamper *et al*., 1989) from DFR residues for the torso and arms which represent 58% of the total potential dermal exposure. This dermal exposure is reduced even further by the rain suits worn by the workers while topping Brussels sprouts. Assuming 42% of the exposure will occur to the hands when gloves are not worn, the remaining 58% of the potential dermal exposure was reduced 95% (Thongsinthusak *et al*., 1990) by the rain suit and then by 89% (work clothing). The values corrected for clothing are listed in Table 3 which details the Absorbed Daily Dosage (ADD) and Seasonally Absorbed Daily Dosage (SADD) values based on these estimates.

C.2 Harvesting tree fruit

The maximal application rate for chlopyrifos for all fruit trees is 3 lbs/acre with a 28-day pre-harvest interval. Iwata *et al.* (1983) measured chlorpyrifos DFR on oranges and grapefruit for applications of 5 and 10 lbs/acre. A narrow range of initial residues (0.3-0.7 ug/cm^2) and half-lives (2.4-3.4 days) were observed. When trees are sprayed at biweekly intervals these short half-lives and low residues negate any significant addition of earlier sprays to the last spray. Thus the last spray before harvest will determine harvester exposure. Assuming a final spray at the pre-harvest interval (28 days), nine three-day half-lives will pass by harvest. Based on post-spray residue of 0.7 ug/cm^2, DFR at harvest will be 0.001 ug/cm^2 after extrapolating for dissipation.

A single application of chlorpyrifos is permitted on pome and stone fruits as a dormant spray between late December and early February after the trees have dropped their leaves. The first farm worker activity after this treatment can occur from mid-March until the end of April when the developing fruit is thinned by hand. This cultural practice entails the worker knocking off the extra young fruits with a long cane or stick in order to increase the size of the fruits and eliminate the hiding places for codling moth larvae. Since the trees of these crops are deciduous, the exposure to foliar residues for fruit thinners is expected to be negligible.

Harvester transfer factors have been calculated for peach and apple harvesters following azinphosmethyl and phosmet applications (Krieger *et al.*, 1990). The transfer factors for potential dermal exposure for peach harvesters are 24,000 to 54,000 cm^2/hr. Assuming that 10% of these residues penetrate the work clothes to the skin, these values can be transformed to 2,400 and 5,400 cm^2/hr. These are very similar to the dermal transfer factor of 7,000 cm^2/hr for nectarine harvesting (Schneider *et al.*, 1990). Based on a dermal transfer factor of 7,000 cm^2/hr and residues of 0.001 ug/cm^2, harvester dermal exposure in 8 hours would be 56 ug/day or 0.80 ug/kg/day. Table 3 shows ADD and SADD values based on this estimate.

C.3 Cotton Scouting

A transfer factor (for potential dermal transfer) for cotton scouts has been derived from several reviews by Dong (1990). This factor (11,610 cm^2/hr) can be combined with observed cotton residues to estimate post-harvest worker exposure for cotton scouts. The soonest that cotton scouts can enter a treated field is 24 hours after application. Several studies have found dissipation half-lives of chlorpyrifos on field cotton as low as one day (Buck *et al.*, 1980; Ware *et al.*, 1978 and 1983) and as high as 3 days (from Veierov, et al., 1988, for potted cotton). A three-day half-life was used for the estimation of occupational exposure for cotton scouts. Based on an initial deposition of 1.8 ug/cm^2 (Buck *et al.*, 1980; Ware *et al.*, 1978 and 1983), the DFR present 24 hours post-application was 1.45 ug/cm^2. Cotton scouts are expected to spend at most 6 hours walking in treated fields, since part of their time is spent traveling between fields. This exposure period would yield a maximum dermal exposure (assuming 10% clothing penetration) of 8,359 ug/day or 119 ug/kg/day. Table 3 shows dermal exposure, ADD and SADD values based on this estimate.

TABLE 3. Normalized Absorbed Dosages for Workers Exposed to Chlorpyrifos Residues Post-Application

Work task	Dermal Exposure ug/kg/d	ADD[a] ug/kg/d	SADD ug/kg/d
Sprout topping[b] day 1	169	16.2	2.16
Tree fruit harvesting[c]	0.80	0.08	0.05
Cotton scouting[d]	119	11.5	1.54

Brodberg and Haskell, WH&S, 1993

Estimates are made for workers wearing standard work clothing: long-sleeved shirt and pants, shoes, and socks. Exposure via inhalation is not included in these estimates because no air values during these work tasks are available and other studies have demonstrated insignificant inhalation exposure for reentry workers. An average worker weight of 70 kg is assumed.

[a] Calculations of ADD are based on dermal absorption of 9.6%.

[b] For workers topping sprouts days after the last chlorpyrifos application: ADD is based on 8 hours of exposure per day; SADD is based on 12 exposure days in a 90-day use season (Haskell and Thongsinthusak, 1992a).

[c] For workers harvesting tree fruit: ADD is based on 8 hours of exposure per day; SADD is based on 93 exposure days per 150 days use season (Haskell, 1991b). The number of exposure days was estimated from information obtained from conversations with farm advisors, County Agricultural personnel, and various publications from the Federal State Market News Service and the California Tree Fruit Agreement.

[d] For workers scouting cotton: ADD is based on 6 hours of exposure per day; SADD is based on 7 exposure days in a 52-day use season (Haskell and Thongsinthusak, 1992b).

D. **Indoor Human Exposure**

Because of the extensive indoor residential use of chlorpyrifos, human indoor non-occupational exposure to this chemical has been given much attention recently by several investigators (Berteau *et al.*, 1989, McDonald, 1988, Fenske *et al.*, 1990). Indirect estimation of potential exposure from residues found on the carpet and in the air following application has been made by these investigators. Infants' exposure has been the focus of this attention primarily for being more routinely exposed to indoor surfaces treated with chlorpyrifos than adults.

The U.S. EPA conducted a large-scale non-occupational pesticide exposure study (NOPES) that identified chlorpyrifos among the most commonly found pesticides in non-occupational settings (Immerman *et al.,* 1990). Chlorpyrifos concentrations in NOPES were much lower compared to the concentrations found soon after a residential application. Therefore, exposure data generated from these studies will not be presented in this document.

There are other studies that estimated infant exposure from infants' movements and activities simulated by human subjects exposed to treated carpet. These latter studies are more physiologically and exposure monitoring-based and are used in the following exposure assessment.

D.1 Exposure of Infants to Chlorpyrifos: the First Study

In the first study, attempts were made to simulate infants' movements by allowing substantial body contact to the treated floor in a reproducible fashion (Ross e*t al*., 1990, 1991, 1992). Five human volunteers were instructed to follow Jazzercise^{TM} routines and stretches on carpeted floors treated with 0.5% chlorpyrifos foggers. The treatments were made per label instructions. Several rooms were used for this study. Each test room was identified and treated based on expected reenry time. Each room was vented two hours after the treatment for 30 minutes. Air conditioners were turned off only during the treatment period. Cotton gauze pads (58 cm^2) and aluminum sheets (400 cm^2) were placed near the corner of each room to measure residue fallout on the floor. Gauze pad and aluminum sheet samples were collected at various time intervals during the study in rooms reserved for study of air and surface dissipation. In addition to the underclothing, each participant wore clothing dosimeters consisting of a pair of tights, long-sleeved t-shirt, cotton gloves, and cotton socks to estimate potential dermal exposure. Clean clothing dosimeters were worn by the participants when entering each test room. The dosimeters were collected at the end of the routines and stretches that lasted about 20 minutes in each room. Air samples were also taken at various times during this study, using an air sampler connected to a solid resin air sampling tube of XAD-2 at 9 inches from the treated surface. Spiked samples of different media were prepared during the study to determine recoveries. All samples were placed on dry ice. Samples were extracted and analyzed for clorpyrifos and its oxon, using a gas chromatograph equipped with an electron capture detector.

Spiked samples demonstrated recoveries from deposition and clothing dosimeters ranging from 95% to 105%. Chlorpyrifos levels in all samples exceeded the minimum detection limits, but no chlorpyrifos oxon was detected in any samples. Chlorpyrifos levels in the air declined rapidly for 6 hours following venting (Time-Weighted-Average, TWA = 14.0 ug/m^3) and then stabilized for an additional 10 hours (TWA = 6.5 ug/m^3). Fallout residues were approximately 2 ug/cm^2 on the gauze pads and aluminum sheets immediately following venting. Residues dissipated more rapidly from aluminum sheets than gauze pads, which may be due to inhanced volatilization from a nonabsorptive aluminum surface. Residue transferred to the clothing dosimeters declined over time. Much of the exposure occurred on feet (26%) and legs (34%). Hands contributed 14% to the total potential dermal exposure.

D.1.1 Inhalation Route

Infants' ADD from the inhalation route was calculated based on a TWA chlorpyrifos concentration of 6.5 ug/m^3 that was observed 6 to 12 hours post-application. The reentry interval for children is six hours post-application. Assuming six hours of continuous activity and 18 hours of rest for a one-year old infant, the ADD from the inhalation route can be calculated as follows:

Chlorpyrifos concentration in the air	=	6.5 ug/m^3
Infant breathing rate during activity[a]	=	0.25 m^3/hour
Infant breathing rate during rest[a]	=	0.09 m^3/hour
Inhalation uptake[b]	=	50%
Body weight[a]	=	10.5 kg

Inhalation exposure (ADD)= (6.5 ug/m^3)(3.12 m^3/day)(50%)/10.5 kg = 1.0 ug/kg/day

D.1.2 Dermal Route

Infants' ADD from the dermal route was calculated based on the area under the curve for cumulative exposure to chlorpyrifos residues of 11.2 mg/adult that was observed on clothing dosimeters, 6 to 12 hours post-application. It was assumed that the infant would not have any clothing protection and significant dermal exposure would not occur during the rest period. ADD from the dermal route can be calculated as follows:

Chlorpyrifos residues on dosimeters	=	11.2 mg/person/day
Infant/adult body suface area[a]	=	3,925 cm^2/17,700 cm2 = 0.222
Dermal absorption rate[c]	=	9.6%

Dermal exposure (ADD)= (11,200 ug/day)(0.222)(9.6%)/10.5 kg = 22.7 ug/kg/day

D.1.3 Oral Route

Infants' ADD from the oral route was assumed to be contributed by residues on hands. It was observed in this study that 14% of the total dermal exposure occurred on hands. Assuming that 50% of residues on hands would be ingested and totally absorbed by a one-year old infant, the ADD from the oral route can be calculated as follows:

Oral ingestion (ADD)- (11,200 ug/day)(0.222)(14%)(50%)/10.5 kg = 16.6 ug/kg/day

D.1.4 Total Exposure

Infant's total ADD from fogger application   =   40.3 ug/kg/day

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Formoli, WH&S, 1992

[a] Snyder *et al.*, 1974
[b] Raabe, 1988
[c] Estimated dermal absorption in this document

D.2 Exposure of Infants to Chlorpyrifos: the Second Study

The second study estimated indoor exposure of infants following an indoor broadcast application of a 0.5% chloropyrifos emulsion (Vaccaro *et al.*, 1991). Exposure was monitored both directly from urinary excretion of exposed volunteers and indirectly by physicochemical evaluation of carpet residue fallout, residue transfer, hand residues, and air residue monitoring. A total of 8 carpeted rooms at two houses were treated with Dursban® LO by a certified applicator per label instructions. The rooms were ventilated for two hours following the application. Gauze pads (4" x 4") and aluminum sheets (3" x 3") were randomly laid on the carpet prior to the treatment. Gauze pad and aluminum sheet samples were collected at various intervals during the study to measure residue fallout and dissipation. Carpet surface wipe samples were taken at various intervals during the study to estimate residue transfer to body surface. Air samples were also taken at a height of 15 inches from the floor (infant breathing zone) during the study to measure potential inhalation exposure.

Six healthy male adult volunteers were instructed to simulate prescribed infant movements such as crawling, playing with blocks, walking, and lying on the back or abdomen in the treated rooms. Each participant wore only a pair of bathing trunks to simulate an unclothed infant wearing only a diaper. The participants entered the rooms after the 2-hour drying period (ventilation) and performed the prescribed movements for 4 hours. At the end of the 4-hour activity, hand rinses were collected from each participant using an anionic surfactant, and they were allowed to take showers. All urine voids were collected at pre-exposure and each day for five days following exposure. Blood samples were taken pre-exposure to establish cholinesterase baseline and 24 and 48 hours following exposure.

All samples were stored on dry ice following collection. Gauze pad, aluminum sheet, and wipe test samples were extracted with isooctane and analyzed using a gas chromatograph equipped with an electron capture detector. Urine samples were analyzed for creatinine and 3,5,6-TCP. Pre-exposure urine samples were spiked with 3,5,6-TCP and stored with other urine samples. Spiked samples showed at least 90% recoveries. The results of urinary 3,5,6-TCP were reported as chlorpyrifos equivalents after correction for molecular weight difference and incomplete (72%) urinary excretion. Blood samples were analyzed for plasma cholinesterase.

Indoor airborne chlorpyrifos concentration 2 and 4 hours after the application averaged 10.9 ug/m^3. The average of airborne concentration observed at 8, 12, and 24 hours after the application was 12.3 ug/m^3. Airborne chlorpyrifos concentration dropped gradually to 4.2 ug/m^3 at 48 hours post-application. Average floor fallout residues were 6.7 ug/cm^2 two hours after the application and 4.4 ug/cm^2 eight hours after the application. Wipe test samples contained 0.03 ug/cm^2 and 0.02 ug/cm^2 chlorpyrifos residues two hours and 4 hours after the application. Average hand residues after 4 hours of activity was 474 ug/adult.

Infant exposure was extrapolated from the exposure that was estimated for each volunteer using residue fallout, wipe test, hand rinse, and air sampling data. The factors that are described in Snyder *et al.* (1974) for adult and for a one-year old infant and dermal absorption of 3% were used in the extrapolations. An infant's ADD was estimated to be 20.5 ug/kg/day. Dermal exposure was calculated based on residues found in the wipe tests. The wipe samples indicated an average residue transfer factor of 0.3%. This is a lower rate of transfer compared to a cotton glove press study that resulted in a 1.03% transfer rate for chlorpyrifos (Roberts, 1989). It is much lower than the transfer rate to clothing dosimeters seen in the study discussed previously (average 13%).

The more interesting part of this study is the direct measurement of chlorpyrifos internal dose from residues found in urine samples. The direct estimate of internal dose in this study is more reliable than the indirect estimation of absorbed dosage using passive dosimetry. It represents actual exposure and eliminates errors developed from many assumptions and extrapolations associated with the indirect estimation of absorbed dosage in this study. Chlorpyrifos urinary excretion for each participant is shown in Table 4. An infant's absorbed dosage from all routes (oral, dermal, inhalation) was estimated to be 21.2 ug/kg. This estimate is the result of 4 hours of exposure, since the participants were exposed for only 4 hours. For consistency a daily 6-hour activity and 18-hour rest period for a one year old infant is assumed (Ross *et al.*, 1992). Based on this assumption, a one year old infant's ADD following indoor broadcast application of chloropyrifos can be calculated as follows:

Absorbed dosage during 4 hours of activity	=	21.2 ug/kg
Absorbed dosage during 2 additional hours of activity	=	10.6 ug/kg
Absorbed dosage during 18 hours of rest from inhalation exposure only[a]	=	0.9 ug

Infants' ADD from broadcast application = 32.7 ug/kg/day

Formoli, WH&S, 1992

[a] Based on average airborne residues of 12.3 ug/m^3 that was observed at 8, 12, and 24 hours post-application, infant breathing rate of 0.09 m^3/hour at rest, and 50% inhalation uptake.

Plasma cholinesterase levels for each participant are shown in Table 5. Individual # 6 with depressed plasma cholinesterase levels was reported ill with high fever just prior to the beginning of the activity due to acute influenza.

Adults' ADD is expected to be much lower than that of infants. Actual experience with adult exposure at several times the label application rate with chlorpyrifos foggers demonstrated very low exposure in conjunction with normal indoor activities (Krieger *et al.*, 1991). The potential dermal and oral exposure of adults to indoor chloropyrifos is reduced significantly compared to infants. This is mainly due to their normal behavioral differences from infants (less hand to mouth contact and less floor contact), tendency to wear more clothing, and reduced body surface area to body weight ratio. A mean absorbed dosage of 11.5 ug/kg was observed in this study (column 2 of Table 4) for adults after four hours of exposure. An ADD of 17.5 ug/kg/day would be a conservative estimate after correction for six hours of daily activity and 18 hours of rest for an adult exposed to an indoor application of chlorpyrifos.

TABLE 4. Chlorpyrifos Urinary Excretion Following Four Hours of Indoor Exposure.

Participants	Dermal + Inhalation observed Adult	Dermal + Inhalation calculated[a] Infant	oral[b] Infant	Total Infant
	(ug/kg)			
1	12.8	16.6	3.6	20.2
2	21.3	27.7	7.6	35.3
3	6.6	8.6	4.4	13.0
4	6.2	7.3	4.0	11.3
5	19.3	22.7	7.5	30.2
6	8.4	9.6	7.6	17.2
Average	11.5$\pm$6.5	15.4$\pm$8.4	5.8$\pm$2.0	212$\pm$9.6

Formoli, WH&S, 1992

[a] Corrected for body surface ratio to body weight of an infant to that of an adult.

[b] Hand exposure from rinses corrected for an infant hand surface area to that of an adult (1/4) and assuming that 50% of residues on both hands to be ingested by an infant.

TABLE 5. Plasma Cholinesterase Levels (Mu/mL) of Each Participants.

Subject	Baseline	24 hours post-application (%)[a]	48 hours post-application (%)[a]
1	3996	4209 (105)	3361 (84)
2	5326	5463 (102)	5587 (105)
3	3603	4066 (113)	4015 (111)
4	3829	3973 (115)	3582 (93)
5	3371	3888 (115)	3322 (98)
6[b]	4666	4170 (89)	3485 (75)

Formoli, WH&S, 1992

[a] % of baseline
[b] Ill with high fever

D.3 Exposure of Adults from an Application of a Household Aerosol Can

Human exposure to chlorpyrifos as a consequence of an application of a household aerosol can for spot treatments was assumed equivalent to the exposure of an applicator spraying a 15-ounce aerosol can of propoxur. Based on a propoxur applicator exposure study, the dermal and respiratory exposure of an applicator spraying one 15-ounce can (1% propoxur) was estimated at 850 ug/person and 30 ug/person, respectively (Sanborn, 1993). Assuming a dermal absorption of 9.6% and inhalation uptake of 50% for chlorpyrifos, the estimated ADD for a 70-kg adult person will be 1.4 ug/kg/application day.

Table 6 summarizes indoor exposure estimates of infants and adults from the studies conducted by Ross *et al.* (1992) and Vaccaro *et al.* (1991). Even though different methods were used to derive the exposure estimates, namely clothing dosimeters and biological monitoring, the exposures of both infants and adults from these two studies are remarkably similar. This Table also summarizes the exposure of adults to from applying a household chlorpyrifos aerosol can.

TABLE 6. Summary: Absorbed Daily Dosage of Chlorpyrifos in Infants and Adults from Indoor Use and Use of a Household Aerosol Can.

	ADD[a] (ug/kg/day)			
	Inhalation	Dermal	Oral	Total
Infants:				
Ross *et al*. (1992)	1.0	22.7	16.6	40.3
Vaccaro and Nolan (1991)	1.8[b]	22.2[c]	8.7[d]	32.7
Adults:				
Ross *et al.* (1992)	0.9	15.4	1.1	17.4
Vaccaro *et al.*, (1991)[e]	1.5[b]	15.7[c]	0.3[d]	17.5
Adults:				
Application of a household aerosol can	NA	NA	NA	1.4

Formoli, WH&S, 1992

[a] Assumed 6 hours of activity and 18 hours of rest period.
[b] Based on average of 10.9 ug/m^3 residues observed in the air 2 and 4 hours post-application and average of 12.3 ug/m^3 residues observed in the air 8, 12, and 24 hours post-application.
[c] From Table 4 corrected for 6 hours of activity minus estimated dose from inhalation.
[d] Fifty percent of hand residues ingested by infants and 5% of hand residues ingested by adults.
[e] Calculations are similar to that of infants, except using adult inhalation rate of 1.74 m^3/hour for the activity period and 0.44 m^3/hour for the rest period.

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Exposure Estimate of Dog Owners/Groomers to Chlorpyrifos
(Addendum to HS-1661)

January 18, 1994

A. General information

This addendum contains information on chlorpyrifos products for use on dogs and exposure estimates of dog owners/groomers to this chemical. These chlorpyrifos products are intended for use to kill or control fleas, ticks, and sarcoptic mange mites on dogs. As of August 1993, there were 18 chlorpyrifos products registered in California. Chlorpyrifos in these products ranges from 2.5 to 10 percent. Percent of chlorpyrifos as an active ingredient and the number of products in each group are: 3.84% (five), 4.85% (seven), 10% (two), and 2.5% (four). Fourteen products are classified as Toxicity Category III pesticides with a signal word "CAUTION". The remaining four products are Toxicity Category II pesticides with a signal word "WARNING" because these products contain petroleum distillates in the formulation. Some product labels recommend rubber or Neoprene gloves to be worn when these products are used to bathe or dip the dogs. However, most product labels do not require gloves to be worn.

All products are intended for use to kill or control pests on mature dogs and puppies that are three months of age or older. However, some products specify that puppies must be four months or older. All products are not intended for use on cats, sick or debilitated animals, or bitches nursing puppies. For treatment procedure, dilute the product in water and stir or mix well. Then dip, sponge, swab, spray, or pour on dogs liberally to assure that the product penetrates fur down to the skin. There is no need to rinse or wipe, but keep the dogs in warm places to allow solution to dry on animals. The effective period to control fleas is 28-30 days and for ticks is 7-21 days. Treatment of dogs to kill pests cannot be repeated more often than once every 3-4 weeks depending on the products. Furthermore, these chlorpyrifos products cannot be used on animals simultaneously or within a few days (some products specify 30 days) before or after treatment with or exposure to cholinesterase inhibiting drugs, pesticides, or chemicals.

B. Exposure assessment

Exposure studies for dog owners/groomers to chlorpyrifos during pest control by bathing, dipping, swabbing, or sponging dogs are not available from registrants or published literature. Therefore, dose absorbed was estimated by using a model proposed by U.S. EPA (1992). Absorbed daily dosage resulting from inhalation exposure was estimated to be 0.15 ug/kg/hour (Ross *et al.*, 1992). The following assumptions are applied to the estimation of dermal exposure:

1. Log K_{ow} used was 4.288. This log K_{ow} is the mid-range reported by Montgomery (1993) and is similar to the average of 4.97 (Bowman and Sans, 1983).

2. The exposure was estimated for bare hands and forearms. This is the worst case scenario because the product labels specify use with and without rubber gloves. Other parts of the body are assumed not exposed to chlorpyrifos or are protected by clothing, e.g. shirts and pants.

3. Factors used in the estimation of absorbed daily dosage (ADD) for a female are: surface areas of hands is 778 cm^2, and forearms is 985 cm^2, and body weight is 61.5 kg (Thongsinthusak *et al*., 1993).

4. It is assumed that a dog owner/groomer may treat the dogs for a maximum time of one hour per day at an average of 5 minutes per dog. During this time period, 12 dogs may be treated with chlorpyrifos. Dipping time should not exceed 30 seconds as recommended by product labels.

5. It is assumed that dose absorbed (DA) derived from the U.S. EPA model is totally bioavailable.

The U.S. EPA model that was used to estimate exposure has 6 steps of calculations. The final step gives the estimation of dose absorbed per cm^2 per hour of activity. Values of the factors used or obtained using the model are shown below:

Kp = 0.0165 cm/hour (permeability coefficient for chlorpyrifos from water through the skin)
B = 1.94 (dimensionless)
Dsc = 1.377E-8 cm^2/h (diffusitivity of a substance within the membrane)
r = 12.1 hours (lag time)
lsc = 1x10E-3 cm (the diffusion path length)
t* = 67.51 hour (based on the value of B)
b = 3.23 (used to calculate t*)
c = 2.27 (used to calculate t*)
Cv = 0.66 mg/cm^3 (maximum dilution rate)
DA = 0.105 mg/cm^2/hour (dose absorbed)

The exposure estimate of a dog owner/groomer is shown in Table 1.

Table 1. Exposure estimate of dog owners/groomers to chlorpyrifos.

Dose absorbed (mg/person/h)	(Inhalation exposure) ADD (ug/kg/h)	Body weight (kg)	ADD (mg/kg/h)
185	0.15	61.50	3.01

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