

DISSIPATION OF DISLODGEABLE RESIDUE
OF CHLORPYRIFOS AND DDVP ON TURF

By

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ABSTRACT

This study was conducted to evaluate the potential of human exposure to Dichloron^R residues and the necessity of establishing a safe reentry interval after its application on turf grass. Dichloron^R containing 2.6% DDVP and 3.0% chlorpyrifos was applied at 7.96 gallons in 1,290 gallons of water/acre on Kentucky bluegrass lawn at Folsom, CA on October 1, 1984. The highest chlorpyrifos foliar dislodgeable residue detected was 0.14 ug/cm² which is well below the estimated safe value at 0.5 ug/cm². Post-spray irrigation significantly reduced the chlorpyrifos foliar residue. DDVP at 0.10 ug/cm² exceeded the estimated safe level (0.06 ug/cm²) for the first two hours after application. The dissipation rate of DDVP was rapid and not affected by irrigation. Residue level reached non-detectable level (< 1 ug/sample) after 24 hours.

Negligible DDVP in air was sampled at 1.9 ± 0.5 ppb ($\bar{x} \pm SE$), (TLV = 0.1 ppm).

Hence, under moist, breezy, cool fall conditions, Dichloron^R dissipated to below estimated safe-levels two hours post-spray on Kentucky bluegrass.

There are 73 insecticide products registered in California for turf anthro-pod and mollusk pests control (Table 1).

Chlorpyrifos and DDVP are two organophosphorus active ingredients used for the control of insect pests in turf. According to the 1983 Pesticide Use Report in California, turf received 165 applications of chlorpyrifos (611.38 lb ai) and 16 applications of DDVP (47.34 lb ai)^{1/}. There is an increasing trend of chlorpyrifos used; DDVP use fluctuates yearly (Figure 1). These moderately toxic chemicals act by inhibiting acetylcholinesterase (Figure 2). Symptoms of acute poisoning include headache, dizziness, weakness, uncoordination, muscle twitching, tremor, nausea, abdominal cramps, diarrhea, and sweating. Incontinence, unconsciousness, and convulsions indicate very severe poisoning^{2/}.

The increased use of more toxic organophosphorus insecticides on lawn and turf in parks and recreational areas posed concerns for possible hazards for humans and animals potentially exposed to toxic levels of residues, albeit most product labels recommended that pests and children be kept off treated turf until the spray has dried. To safeguard against potential hazards, safe levels of dislodgeable residue have been estimated so that safe reentry interval or reentry precautions can be established^{4/}. The estimated safe levels of dislodgeable foliar residue for chlorpyrifos and DDVP are 0.50 ug/cm² and 0.06 ug/cm², respectively^{3/}.

Turf insecticide hazards were brought to our attention due to a recent alleged poisoning case involving children who were playing on a lawn sprayed with an insecticide containing chlorpyrifos and DDVP. There are three unrestricted household lawn insecticides with this combination (Table 2).

This study reports the methodology for investigating dislodgeable residue on turf grass. The maximum recommended rate for Dichloron^R (see attached label) was applied on Kentucky bluegrass and dissipation of foliar chlorpyrifos and DDVP residues was monitored. Air samples were also taken to determine concentrations of pesticide in air after application.

Methods and Materials

Turf plots were located at Folsom, Sacramento County, California during October 1984. They consisted of pure, healthy and uniform stands of Kentucky bluegrass grown under full sun.

Correlation of Leaf Weight to Surface Area

Twenty leaf-lamina samples ranging from 2 to 18 grams were cut with scissors and weighed to the nearest centigram. The single surface leaf area was measured with a LI-3100 leaf area meter (LI-COR, Nebraska) to within ± 0.001 cm² for each sample of known fresh weight. A linear regression of surface area (both sides) to fresh weight was generated from the data.

Dislodgeable Residue Sampling

Six 2' x 8' (16 square feet) plots were selected, marked and sprayed with Dichloron^R at 0700 hours (ambient temperature 13°C; relative humidity 86%; and a slight breeze of 1-2 mph). Immediately after spraying, three plots were watered in with 1/2 inch of water. The chemical was applied at the maximum recommended rate with a 2 gallon Hudson back-pack sprayer under low pressure equipped with a nozzle producing coarse droplets (Table 3).

Leaf samples were taken before, immediately after spraying, and at 2, 6, 10, 24, 48, 72 and 96 hours post-spray. Two random samples per plot, each filling an 8 ounce jar (approximately 8 grams of grass), were taken and immediately stored on ice until delivery to the laboratory for accurate weighing and dislodgeable foliar residue analyses for chlorpyrifos and DDVP.

Air Sampling Procedures

Air samples were collected by drawing air through an XAD-4 sampling tube with a MSA Model 1 Fist-Flo^R personnel air pump. The air pumps ran for 15 minutes at the rate of 1 litre/minute as calibrated with a Kurz^R 540-S flow calibrator. Two samples/treatment were drawn at pre-spray, 0, 1, 2, 6 and 10 hours post-spray.

Residue Analyses for Dislodgeable Residues Extraction

Leaf samples were rotated three times for 30 minutes each at 30 cycles/minute in: i) 50 ml of water with 0.2 ml of 2% Sur-Ten Solution; ii) 50 ml of water with Sur-Ten; and, iii) 50 ml water only. The 150 ml aqueous solution was extracted three times with 50, 25, and 25 ml of ethyl acetate. The solvent was filtered through sodium sulfate and held in freezer prior to cleanup and analysis.

Gas Chromatograph Conditions

G.C.: HP 5880-A

Column: 25 x 0.2 mmid. SE-54 coated fused silica capillary column.
Pressure 15 psi.

Oven Temperature: 170° - 240°C

Injector Temperature: 225°C

Detector Temperature: 250°C

Carrier Gas: 25 ml/min HC

Septum Purge: 2 ml/min

Split Vent: 50 ml/min

Retention Time: DDVP = 2.45 min Chlorpyrifos = 6.58 min

Results and Discussion

The linear regression for Kentucky bluegrass total leaf-surface area to fresh weight was $y = 80.90 x - 13.69$ ($r = 0.99$) and forced regression through the origin was $y = 79.28 x$ ($r = 0.99$) (Figure 3). This correlation gave a quick and accurate method for estimating leaf surface from known fresh weight of sample and enabled us to calibrate the dislodgeable residue (ug) per surface area of leaf (cm^2) without tedious measurement of leaf area each time.

Dichloron^R applied at the maximum rate of 7.96 gallons/acre in 1,290 gallons of water was well below the estimated safe dislodgeable foliar residue level of 0.5 ug/cm^2 for chlorpyrifos. The highest level attained was $0.14 \pm 0.01 \text{ ug/cm}^2$ ($\bar{x} \pm \text{SE}$) immediately after spraying. Dissipation rates up till 48 hours was significantly greater in the irrigated plot versus the non-irrigated plot. Chlorpyrifos dissipated rapidly to 0.009 and 0.013 ug/cm^2 , respectively in 96 hours (Figure 4). Irrigating with 1/2 inch of water after spraying significantly reduced the residue level on foliage. The water washed chlorpyrifos into the thatch and soil zone for control of most insects, especially soil grubs and sodweb worm.

Residual chlorpyrifos was formulated with DDVP of high vapor pressure (0.01 mm Hg at 30°C) for its fumigation action. Besides its toxicity, DDVP probably also irritates insects into motion, hence exposing them to better contact action of chlorpyrifos.

Immediately post-application, after the lawn had dried (< 2 hours), the DDVP dislodgeable foliar residue level was at 0.10 ug/cm^2 , which exceeded the estimated safe level of 0.06 ug/cm^2 (Figure 5). This level dropped rapidly below safe-level after two hours and the residue was non-detectable after 24 hours (minimum detectable level 1 ug/sample). There was no significant difference in dissipation of dislodgeable residues between post-spray irrigated and non-irrigated plots. Only DDVP was detected in air samples immediately post-spray at $1.9 \text{ ppb} \pm 0.5$, which is well below TLV of 0.1 ppm.

Under cool, breezy and moist fall conditions in Northern California, Dichloron^R dissipated to below estimated safe levels after two hours in Kentucky bluegrass.

TABLE I

Classification of Active Ingredients
of 73 Registered Insecticides Used on
Turf Grass Anthropod and Mollusk Pests
in California, 1984

<u>Organophosphorus</u>	<u>Carbamates</u>
Acephate	Aldicarb
Chlorpyrifos	Carbaryl
Diazinon	Carbofuran
Disulfoton	Mexacarbate
Dichlorvos	Methiocarb
Dicrotophos	Methomyl
Malathion	
Oxydemeton-methyl	<u>Chlorinated hydrocarbons</u>
Methyl parathion	Dicofol
Mevinphos	Lindane
Monocroptophos	Toxaphene
Parathion	
Phosmet	<u>Brominated hydrocarbon fumigant</u>
	Methyl bromide
	<u>Inorganics</u> <u>Other</u>
	Cayolite Methylaldehyde

TABLE II
California Registered Turf Insecticides
Containing DDVP

<u>Products</u>	<u>EPA Reg. No.</u>	<u>% DDVP</u>	<u>% Dursban</u>	<u>Maximum Rate #ai/A</u>		<u>Recommended Water gal/A</u>
				<u>DDVP</u>	<u>Dursban</u>	
SMCP Dursban Plus Turf Insecticide (Dettelbach)	6720-203 AA	3	12.2	0.25	1.00	1,300
Professional Orkinban Lawn Insecticide	6754-68 AA	3.1	12.8	0.25	1.00	1,300
National Chemsearch Dichloron	1769-233 ZA	2.6	3.0	1.59	1.83	1,290

TABLE III

Dichloron Used at Recommended Rate
of 1 Gallon in 160 Gallons of
Water for 5,470 sq. ft. of
Lawn

<u>Chemical Components</u>	<u>Percent</u>	<u>Weight Equivalent</u>	<u>Rate ai/A</u>	<u>Formulation</u>	<u>Product/Plot (16 sq. ft.)</u>
Chlorpyrifos	3%	0.23 lb/gal	1.83 lb	7.96 gal/A	11.07 ml
DDVP	2.6%	0.20	1.59 lb		
Related Compounds	0.2%				
Heavy Aromatic Naptha	90.0%				
Water Used				1,290 gal/A	1,793 ml

Figure 1

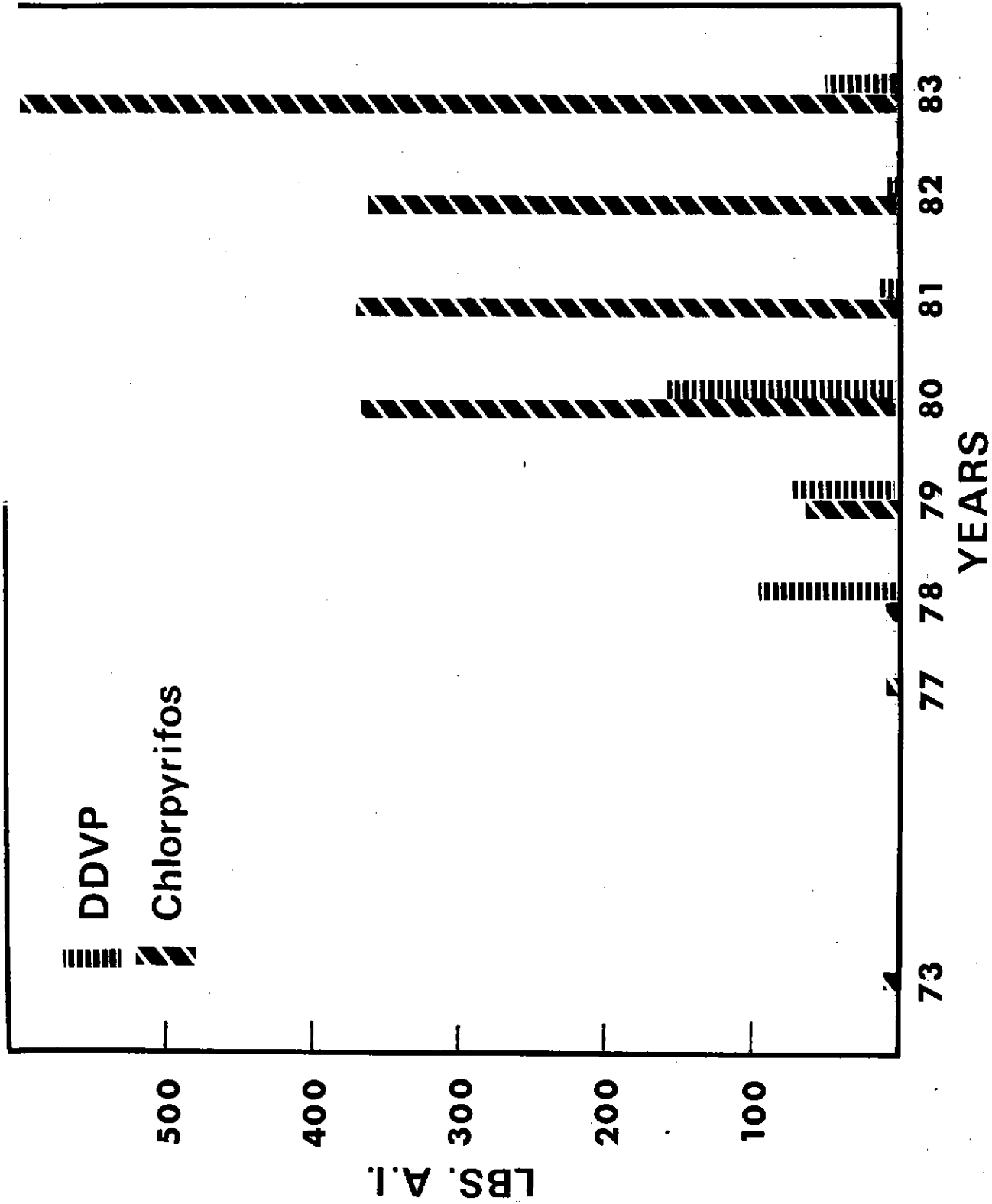


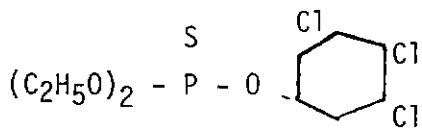
Fig. 1 Trend of DDVP and chlorpyrifos used on turf and landscape area in California. Data from Pesticide Use Report by Commodity 1973-1983, California Department of Food and Agriculture.

Figure 2

CHEMICAL STRUCTURES AND TOXICITY DATA
FOR CHLORPYRIFOS AND DDVP
(5), (6)

Chlorpyrifos

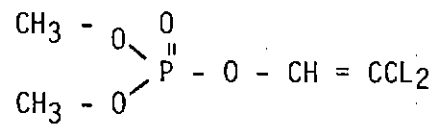
0,0-Diethyl
O-(3,5,6-trichloro-2-pyridinyl)
phosphorothioate, Dursban^R, Lorsban^R



LD₅₀: Oral 82-155 mg/kg
Dermal 202 mg/kg
TLV 0.2 mg/m³
STEL 0.6 mg/m³
Calculated Safe
Level of Residue
on Foliage: 0.5 ug/cm²

DDVP

2,2-Dichlorovinyl
dimethyl phosphate;
Dichlorvos, Vapona^R



56-80 mg/kg
75-107 mg/kg
1 mg/m³
3 mg/m³
0.06 ug/cm²

Figure 3

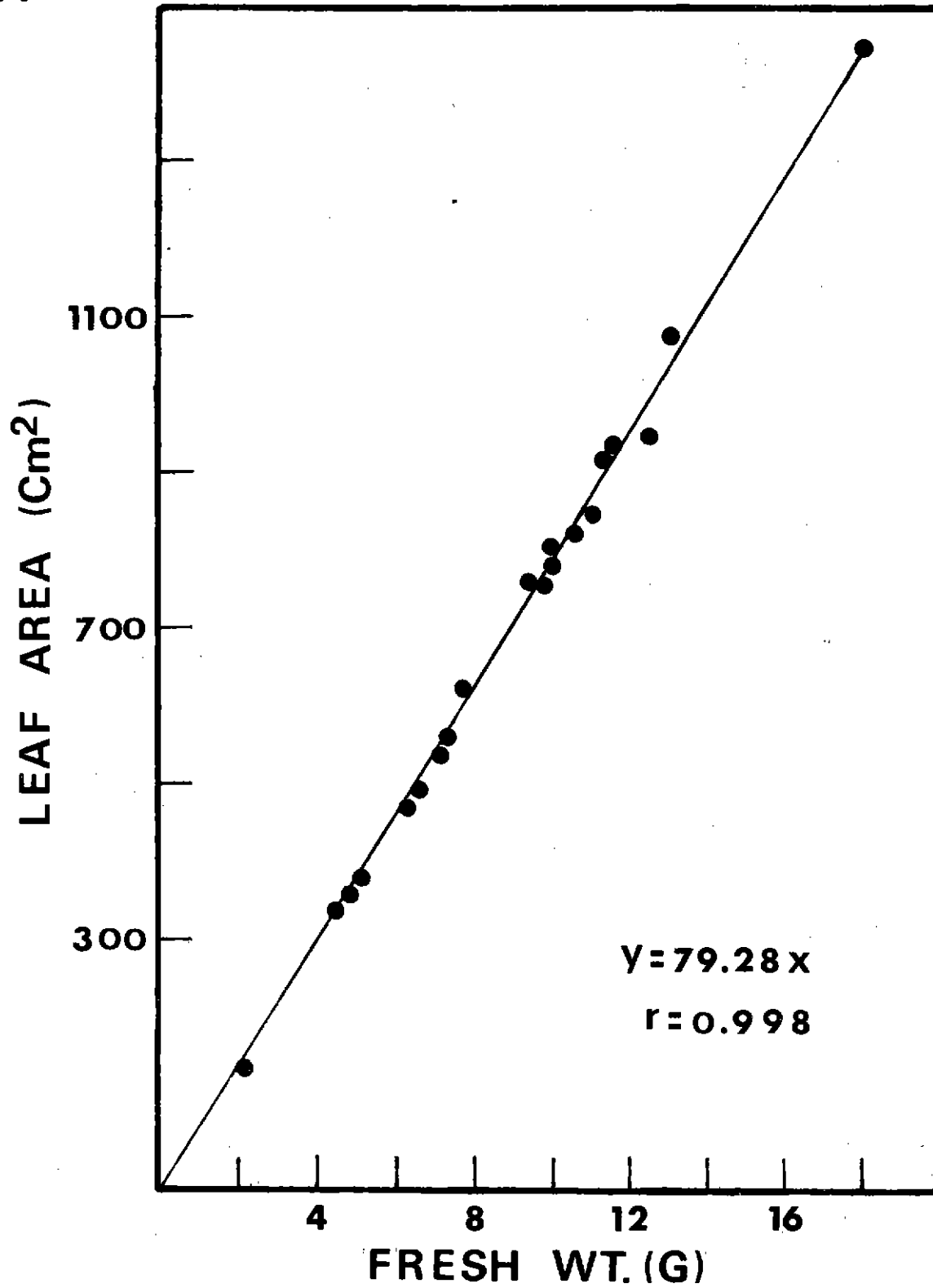


Fig. 3 Regression of Leaf Surface area (both sides) to fresh weight of Kentucky blue grass, Folsom, CA October 1984.

Figure 4

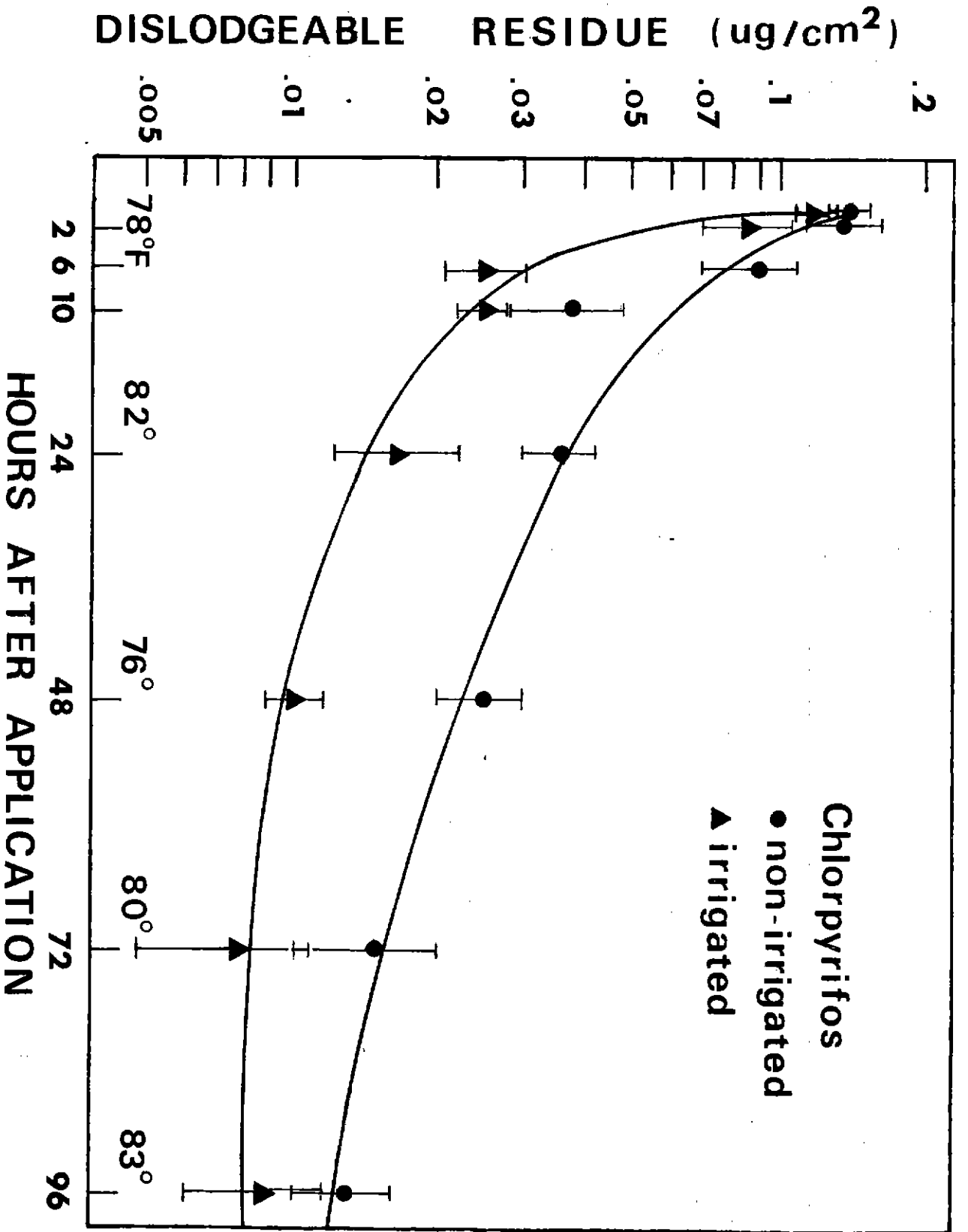


Fig. 4 Dissipation of foliar dislodgement residue for chlorpyrifos (means + 95% confidence interval) in post-application irrigated and non-irrigated plots. Foliosom, CA 1984. Maximum daily temperature shown above x-axis.

Figure 5

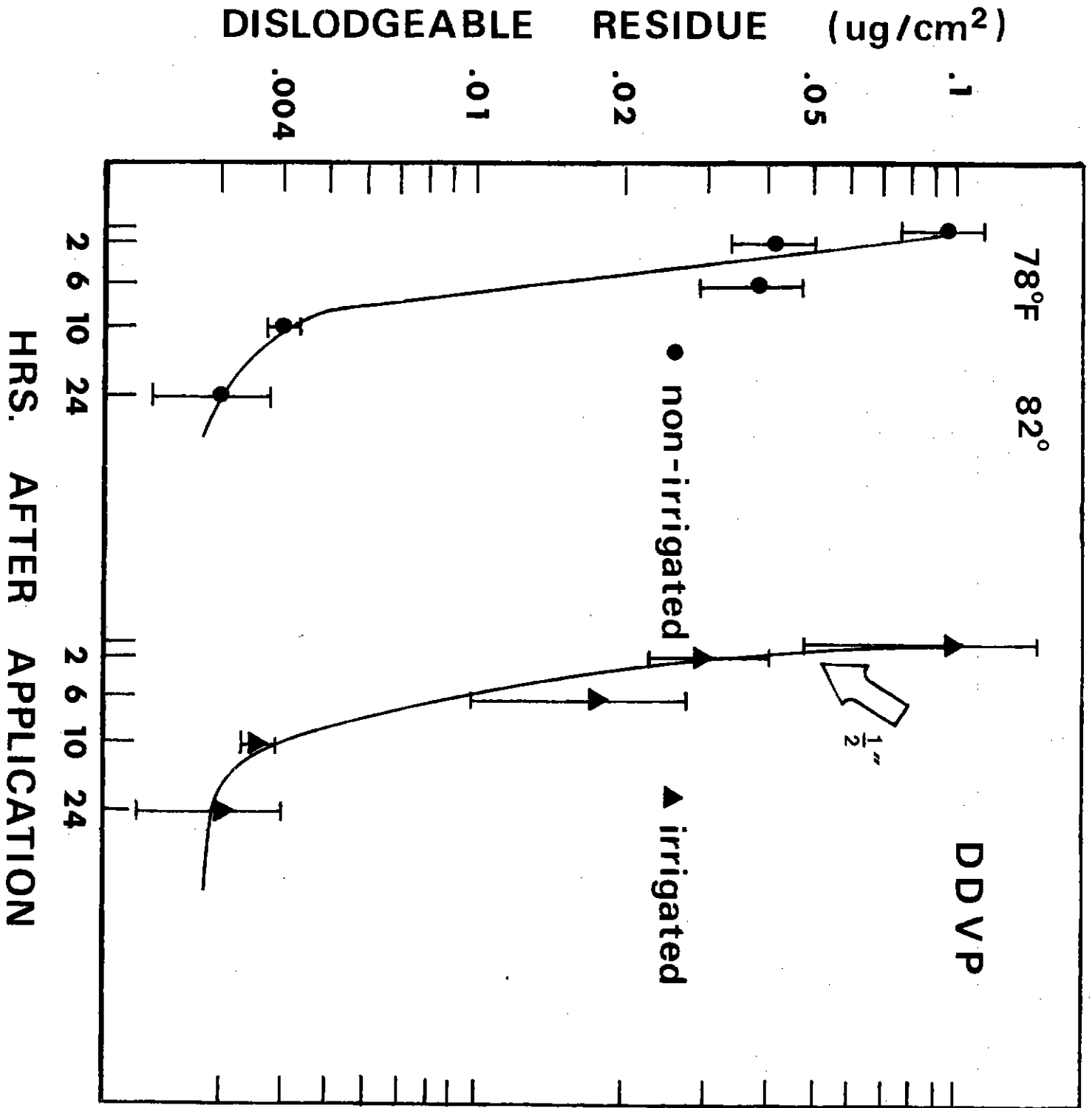


Fig. 5 Dissipation of foliar dislodgeable residue for DDVP (means + 95% confidence interval) in post-application irrigated and non-irrigated plots. Folsom, CA 1984. Horizontal line at $0.06 \mu\text{g}/\text{cm}^2$ indicates estimated safe re-entry level. Temperatures are daily maximum.

REFERENCES

1. Anonymous - Pesticide Use Report by Commodity 1970-1983. State of California, Department of Food and Agriculture. Pesticide Registration and Agricultural Productivity.
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NATIONAL

DICHLOROBROM

Insecticide

ACTIVE INGREDIENTS:

Chlorpyrifos 10.0 dethylo 0-13.5.6 Trichloro-2-Pyridyl	3.00%
Phosphorothioate	2.80%
2,2-dichlorovinyl dimethyl phosphinate	0.20%
Related Compounds	90.00%
Heavy Aromatic Naphthalene	4.20%
TOTAL	100.00%

TOTAL 100.00%
 *U.S. Patent No. 5,244,586
 Equivalent to 0.20 pounds per gallon
 **Equivalent to 0.20 pounds per gallon
 Controls pests of houseplants, turf and Ornamental Plants. Also recommended for Mosquito Control, Houseflies and area control of ticks and chiggers.

KEEP OUT OF REACH OF CHILDREN

WARNING

(See right panel for additional warnings)
 EPA Reg. No. 1769-233

NOT FOR RESALE OR RESIDENTIAL USE AND STORAGE, UNLESS APPLIED AND STORED BY SERVICE PERSONS.

PRECAUTIONARY STATEMENTS

HAZARDS TO HUMANS AND DOMESTIC ANIMALS
 WARNING: Keep out of the reach of children. May be lethal if swallowed, inhaled or absorbed through the skin. Do not breathe vapors or sprays. Mist, smoke, or concentrate in a well-ventilated area. Causes eye and skin irritation. Do not get in eyes, on skin or on clothing. Wash contaminated clothing. Wear a pesticide respirator, jointly approved by the Mining, Enforcement and Safety Administration (formerly the U.S. Bureau of Mines) and by the National Institute for Occupational Safety and Health under the provisions of 30 CFR Part II.

NET CONTENTS:

NATIONAL CHEMSEARCH
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STATEMENT OF PRACTICAL TREATMENT

It is recommended that you call a physician or poison control center immediately if possible vomiting should be induced under medical supervision. Drink one or two glasses of water and induce vomiting by touching the back of throat with finger. Do not induce vomiting or give anything by mouth to an unconscious person. If inhaled—Remove victim to fresh air. Apply artificial respiration if indicated. If on skin—Remove contaminated clothing and wash affected areas with soap and water. If in eyes—Flush eyes with plenty of water. Call a physician immediately.

NOTE TO PHYSICIAN: Chlorpyrifos and DDBP are cholinesterase inhibitors. Treat symptomatically. Atropine is antidote. 2-PAM is also antidote and may be administered in conjunction with atropine.

ENVIRONMENTAL HAZARDS:
 This product is toxic to fish, birds and other wildlife. Do not apply directly to water. Do not apply when weather conditions favor drift from areas treated. Do not contaminate water by cleaning of equipment or disposal of waste. Slurry and sludge may be killed at application rates recommended on the label. Do not apply where these are important resources. Apply this product only as specified on the label.

This pesticide is toxic to bees exposed to direct treatment or to residues remaining on the treated area. Do not apply when bees are actively visiting the crop. Cover crop or weeds blooming in the treatment area. Applications should be timed to provide the maximum possible interval between treatment and the next period of bee activity.

PHYSICAL OR CHEMICAL HAZARDS:

Do not use, pour, spill or store near heat or open flame.

DIRECTIONS FOR USE

It is a violation of Federal law to use this product in a manner inconsistent with its labeling.

STORAGE AND DISPOSAL:

Do not contaminate water, food, or feed by storage or disposal.
STORAGE—KEEP CONTAINER CLOSED.
PESTICIDE DISPOSAL: Pesticide, spray mixture, or rinse water, that cannot be used according to label instructions must be disposed of according to Federal or approved state procedures under Subtitle C of the Resource Conservation and Recovery Act.
CONTAINER DISPOSAL: Triple rinse (or equivalent). Then offer for recycling or reconditioning, or puncture and dispose of in a sanitary landfill or by other approved state and local procedures.

INDOOR PESTS: For spot application in industrial plants, municipal buildings, schools, hotels, homes, apartments, non-food areas of food handling establishments, hospitals and health care institutions.

NON-FOOD AREAS: Includes garbage rooms, lavatories, floor drains (to sewers), entries and vestibules, offices, locker rooms, machine rooms, boiler rooms, garages, mop closets and storage (after lancing or bottling).

To control cockroaches (including strains resistant to certain other insecticides), ants, clovermites, crickets, fleas, ticks, silverfish, spiders. Use 1 part DICHLOROBROM with 11 parts of water to control light infestations and 1 part DICHLOROBROM with 5 parts of water to quickly reduce heavy infestations. For spot treatment, apply as a coarse spray or with a paint brush to localized areas where these pests are found or normally occur, including dark corners of rooms, and closets (cracks and crevices along walls, along and behind baseboards, beneath and behind sinks, stoves, refrigerators and cabinets, around plumbing and other utility installations). For ants apply to ant trails, also around doors and windows and wherever else these pests may find entrance. For caterpillars, use the 1 to 5 dilution only.

NOTE: A period of 4 to 7 days is normally required for maximum effect on cockroaches. Includes areas for reworking, storage, packing, learning, bottling, wrapping, boxing, preshrinking, wool, waste storage and enclosed processing systems (mills, daires, edible oils presses). Servicing areas when food is exposed and facility is in operation also considered food areas. Mix 1 part DICHLOROBROM with 17 parts water to control light infestations, mix 1 part DICHLOROBROM with 5 parts water to quickly reduce heavy infestation.

Apply in spray, aerosols, directly into cracks and crevices using equipment. Labeled oil dispersing agent should be used in areas between different elements of construction between equipment and tanks, openings leading to walls and hollow spaces in walls, foundation legs and bases, where cockroaches, crickets, fleas, spiders, and spiders. Do not apply to electrical equipment, multiple heating, junction and switch boxes or other electrical equipment because of possible shock hazard.

Label should be taken to avoid depositing the product onto exposed surfaces or introducing the material into the air. Avoid contamination of food or food processing surfaces.

APPLICATIONS OF THIS PRODUCT IN THE FOOD AREAS OF FOOD HANDLING ESTABLISHMENTS OTHER THAN AS A CRACK AND CREVICE TREATMENT ARE NOT PERMITTED.

*Do not use where solvent are confined in room or in operating rooms, nurseries, etc. areas where patients are in danger.

SERVING AREAS: Facilities where prepared foods are served, such as dining rooms, but excluding areas where foods may be prepared or held. Mix 1 part DICHLOROBROM with 11 parts water to control light infestations and 1 part DICHLOROBROM to 5 parts water to quickly reduce heavy infestations. Apply as a spot treatment to selective surfaces such as baseboards, under-equipment, and into cracks and crevices. Avoid treating surfaces likely to be contacted by food. Do not apply when facility is in operation or food are exposed.

WARNING (Pests indoors): For Spot Application Only. Do not use in poultry houses or other animal buildings. Do not spray to contact food, feedstuffs and water supplies. Thoroughly wash dishes and food handling utensils with soap and water if they become contaminated by application of this product. Do not allow children or pets to contact treated surfaces until spray has dried. Remove pets and cover fish bowls (tanks) before spraying.

OUT-OF-DOOR PESTS: Houseflies. To reduce the annoyance of houseflies, dilute DICHLOROBROM at 1 gallon to 11 gallons of water and spray outside surface of windows, door frames, around garbage cans, trash bins, etc. where houseflies are a problem. Repeat treatment when effectiveness diminishes.

LAWN PESTS: To control ants, armyworms, brown dog ticks, chiggers, chinch bugs, cutworms, earwigs, fleas, grasshoppers and sod webworms (lawn moths), dilute 1 gallon of DICHLOROBROM with 320 gallons of water to cover 10,970 sq. ft. Apply as a coarse low pressure spray using suitable application equipment. Thoroughly water immediately after treatment to wash the insecticide into the turf (except for sod webworms). For sod webworms, delay watering or mowing the treated area for 12 to 24 hours after treatment. For best results, the lawn should be moist at the time of treatment, and care should be taken to obtain complete and uniform coverage of pest infested areas. Spray when pests first appear; repeat applications every 7 to 10 days. Do not spray on lawns that are being prepared for sod. Do not apply to lawns that are being prepared for sod. Do not apply to lawns that are being prepared for sod.

ORNAMENTAL PLANTS: To control grassy meads, dogwoods, grasshoppers, mites, springtails and whiteflies on flowers, shrubs, vines, shade and flowering trees and evergreens use DICHLOROBROM at the rate of 1 gallon in 100 gallons of water. To control cutworms, mealybugs, thrips and other insects, use DICHLOROBROM at the rate of 1 gallon in 50 gallons of water. Apply using suitable hand or power spray equipment in a manner to provide complete and uniform coverage of infested plants. Avoid overspraying to the point of excessive runoff. Treat when pests appear and repeat at 7 to 10 day intervals if needed. Note: Do not use on azaleas, camellias, pansies, roses, bushes or variegated ivy because of possible injury to these plants.

WARNING: Lawn and Ornamental Plant Pests: Do not spray food crops. Keep children and pets off treated areas until spray has dried. Keep out of lawn and garden lawn areas and other areas of water. NOTE: Misapplications causing injury to ornamental plants, turf and other areas are the responsibility of the user. Do not use on lawns that are being prepared for sod. Do not use on lawns that are being prepared for sod.

AREA CONTROL OF TICKS AND CHIGGERS: Use DICHLOROBROM to control ticks and chiggers infesting non-crochard trees such as redwoods, loblombs and firs, pines and cypresses, shrubs, pines and other recreational areas where these pests are present and create a nuisance or possible public health problem. Apply DICHLOROBROM in water at the rate of 1 gallon per acre (equivalent to 3 fl. oz. per 1,000 sq. ft.) using a hydraulic sprayer, mist applicator, knapsack sprayer, or other suitable hand or power spray equipment. Treat low underbrush, grassy areas, weeds, and ground surface and debris using enough spray volume to obtain thorough coverage, usually 40 to 100 gallons per acre.

ATTENTION: (Area Control of Ticks and Chiggers) Do not allow public use of treated areas during application or until spray has dried.

DISCUSSIONS: To control mosquito larvae, use 1 gallon of DICHLOROBROM in sufficient water or oil, such as kerosene or fuel oil, to cover 10 to 20 acres of home to medium vegetation and 5 to 10 acres of medium to heavy vegetation. Apply the spray to provide complete and uniform coverage of infested ponds.

To control adult mosquitoes, use 1 gallon of DICHLOROBROM in sufficient water or oil, such as kerosene or No. 2 fuel oil, to cover 10 acres of home to medium vegetation and 5 acres of heavy vegetation.

NOTE: Seller warrants that the product conforms to its chemical description and is reasonably fit for the purposes stated on the label when used in accordance with directions under normal conditions of use, but neither this warranty or any other warranty of MERCHANTABILITY or FITNESS FOR A PARTICULAR PURPOSE, express or implied, extends to the use of this product contrary to label instructions, or under abnormal conditions, or under conditions not reasonably foreseeable to seller, and buyer assumes the risk of any such use.

TO REGISTER:

In Texas call 1-800-442-7950. Outside Texas, call 1-800-527-9821

EPA Est. No. 4140

CA-1 IN-1 NJ-1 PR-1 TX-1

8M311

ACKNOWLEDGEMENT

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