

## Dissipation of Dislodgeable Foliar Residue of Chlorpyrifos and Dichlorvos on Turf

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There are currently 73 insecticide products containing 25 active ingredients registered in California for turf arthropod and mollusk pest control. Chlorpyrifos (o,o-diethyl o-(3,5,6-trichloro-2-pyridiny1) phosphorothioate) and dichlorvos/DDVP (2.2-dichlorovinyl dimethyl phosphate) are two organophosphorus compounds used for the control of insect pests in turf. According to the 1983 Pesticide Use Report in California, turf received 165 applications of chlorpyrifos (277.32 kg ai) and 16 applications of DDVP (21.47 kg ai) (Anon. 1983). There is an increasing trend of chlorpyrifos being used; DDVP, used mostly in combination with other insecticides, fluctuates yearly (Fig. 1). The Pesticide Use Reports reflect primarily use of restricted materials or use by certified pest control operators. Therefore the use of chlorpyrifos and dichlorvos (not being restricted) is probably drastically underestimated. These moderately toxic chemicals (chlorpyrifos rat acute oral  $LD_{50} = 82-155$  mg/kg, dermal  $LD_{50} = 202$  mg/kg; DDVP oral LD<sub>50</sub> = 56-80 mg/kg, dermal LD<sub>50</sub> = 75-107 mg/kg) are acetycholinesterase inhibitors (Gaines 1960,1969). The increased use of toxic organophosphorus insecticides on lawns and turf within parks and recreational areas poses concern to humans and animals that may be potentially exposed to toxic levels of residues; albeit most product labels recommend that pets 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 intervals or reentry precautions can be established (Knaak et al 1980). In California the estimated safe levels of dislodgeable foliar residue to chlorpyrifos and DDVP are 0.5 ug/cm<sup>2</sup> and 0.06 ug/cm<sup>2</sup>, respectively (Maddy et al 1984). 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.

Due to a recent alleged poisoning case involving children who were playing on a lawn treated with chlorpyrifos and dichlorvos, this study was conducted. Dichloron (TM) was selected from at least those lawn insecticides containing chlorpyrifos and dichlorvos registered for home use. This study also reports the methodology

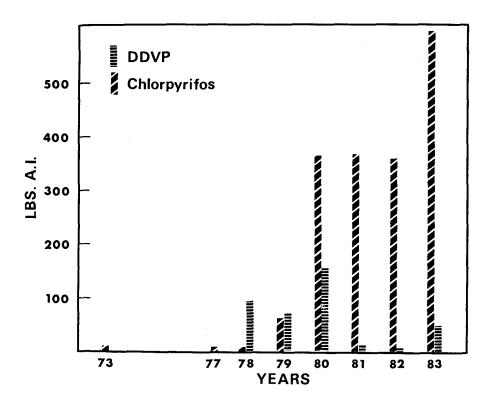


Figure 1. Trend of DDVP and chlorpyrifos used on turf and landscape area in California. Data from Pesticide Use Report by Commodity 1973-1983, California Department of Food and Agriculture.

for investigating dislodgeable residue on turfgrass. The maximum recommended rate for Dichloron(TM) was applied on Kentucky bluegrass and dissipation of foliar and aerial chlorpyrifos and DDVP residues was monitored.

## MATERIALS AND METHODS

Turf plots were located at Folsom, Sacramento County, California during October 1984. They were pure, healthy and uniform stands of Kentucky bluegrass grown under full sun. Six 0.61 m x 2.44 m (1.49 sq m) plots were selected, marked and sprayed at 0700 hours with Dichloron(TM) which contained 2.6% DDVP and 3.0% chlorpyrifos, (ambient temperature 13°C; relative humidity 86%; and a slight breeze of 1-3 km/h). The pesticide was applied at the maximum recommended rate (3.79 l of product in 605.67 l of water for 508.18 sq m of lawn) with a 7.57 l Hudson back-pack sprayer equipped with a nozzle producing coarse droplets under low pressure. Immediately after spraying, three plots were watered in with 12.7 mm of water. 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

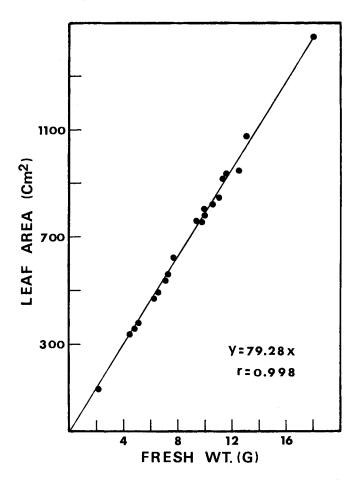


Figure 2. Regression of leaf surface area (both sides) to fresh weight of Kentucky blue grass, Folsom, CA October 1984.

jar (approximately 8 gms. 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.

Dislodgeable foliar residue is measured in weight of residue/ foliar surface area, and since leaf weight is easier to measure than area, a correlation of leaf weight to surface area for Kentucky bluegrass was preestablished. A linear regression of surface area (both sides) to fresh weight was generated from 20 leaf-lamina samples ranging from 2 to 18 grams which were cut 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  $\pm$  0.001 cm<sup>2</sup> for each sample of known fresh weight.

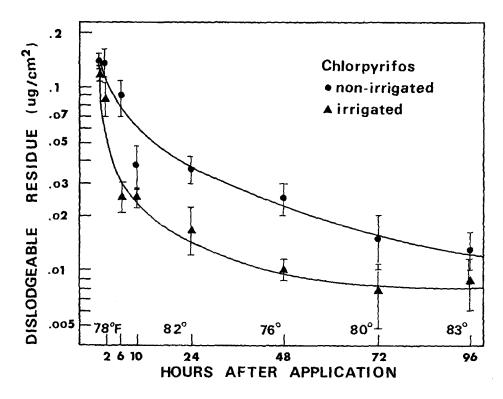


Figure 3. Dissipation of foliar dislodgeable residue for chlorpyrifos (means + 95% confidence interval) in post-application irrigated and non-irrigated plots. Folsom, CA, 1984. Maximum daily temperature shown above x-axis.

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

Dislodgeable residues were extracted by rotating the leaf samples three times for 30 minutes each at 30 cycles/minute in: 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 dried over sodium sulfate and analyzed by HP 5880-A gas chromatography with a 25 x 0.2 mm id, SE-54 fused silica coated capillary column. Sample solutions and appropriate standards were injected using the following instrument parameters: pressure 15 psi oven temperature 170 - 240°C; injector temperature 225°C; detector temperature 250°C; helium carrier gas flow 25 ml/min; septum purge 2 ml/min and split vent 50 ml/min; retention time DDVP = 2.45 min and chlorpyrifos = 6.58 min. The detection limit of chlorpyrifos and DDVP was 1 ug/sample.

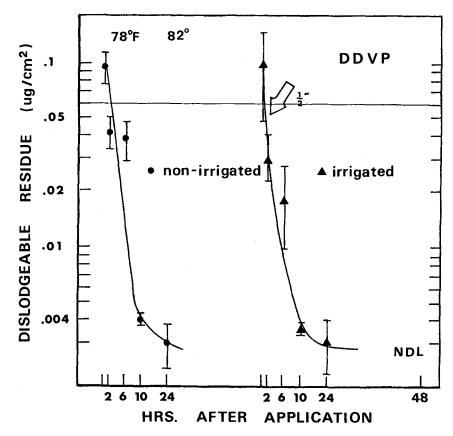


Figure 4. Dissipation of foliar dislodgeable residue for DDVP (means + 95% confidence interval) in post-application irrigated and non-irrigated plots. Folsom, CA, 1984. Horizontal line at 0.06 ug/cm<sup>2</sup> indicates estimated safe re-entry level. Temperatures are daily maximum.

## RESULTS AND DISCUSSION

The linear regression for Kentucky bluegrass total leaf-surface area to fresh weight was Y = 80.90X - 13.69 (r = 0.99) and forced regression through the origin was Y = 79.28X (r = 0.99) (Fig. 2). This correlation gave a quick and accurate method for estimating leaf surface area from known fresh weight of sample and enabled us to calculate the dislodgeable residue (ug) per surface area (cm<sup>2</sup>) without tedious measurement of leaf area each time.

Dichloron(TM) applied at the maximum rate of 74.45 l/ha in 4,883 l of water was well below the estimated safe dislodgeable foliar residue level of 0.5  $\text{ug/cm}^2$  for chlorpyrifos. The highest level attained was 0.14 + 0.01  $\text{ug/cm}^2$  (x SE) immediately after spraying. Dissipation rates up to 48 hours were significantly greater in the irrigated plot versus the non-irrigated plot. Chlorpyrifos dissipated rapidly to 0.009 and 0.013  $\text{ug/cm}^2$  respectively in 96

hours (Fig. 3). Post-spray irrigating with 12.7 mm of water as recommended by the label for most turf insect control situations, 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 sod webworm.

Chlorpyrifos, with residual activity, was formulated with DDVP of high vapor pressure (0.01 mm Hg at  $30\,^{\circ}$ C) for its fumigation action. Besides being toxic, DDVP probably irritates the insects causing greater activity, hence exposing them to better contact action to chlorpyrifos.

The DDVP dislodgeable foliar residue level was  $0.10~\rm ug/cm^2$  immediately after postapplication (<2 hours), which exceeded the estimated safe level of  $0.06~\rm mg/cm^2$  (Fig. 4). This level dropped rapidly below the safe level after two hours and the residue was nondetectable after 23 hours (minimum detectable level 1 ug/sample). There was no significant difference in dissipation of dislodgable residues between post-spray irrigated and non-irrigated plots. Only DDVP was detected in air samples immediately post-spray at  $1.9~\pm~0.5~\rm ppb$ , which is well below Threshold Limit Values of  $0.1~\rm ppm$  (Anon. 1983-84).

Under cool, breezy and moist autumnal conditions in northern California, chlorpyrifos and dichlorvos dissipated to below estimated safe levels after two hours in a Kentucky bluegrass lawn.

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