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Effect of Perforated Plastic Row Covers on Residues of the Herbicide DCPA in Soil and Broccoli

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Various types of clear or tinted, perforated plastic films are increasingly used as crop row covers in production of numerous fruit and vegetable crops (Rickard 1979). In temperate climates the modified environment under these covers permits earlier planting and promotes early-season growth but it also favors aggressive weed growth necessitating the use of herbicides. DCPA (dimethyl tetrachloroterephthalate, tradename Dacthal) is a post-plant, soil-applied herbicide that is widely used in many horticultural crops. DCPA is acknowledged as being strongly adsorbed to soil organic matter and essentially immobile in soil (Helling et al. 1971). It is degraded by soil microorganisms (Tweedy et al. 1968) and is not being appreciably affected by photodecomposition or volatilization (Weed Sci. Soc. Amer. 1983). However, recent studies have reported significant volatilization losses of DCPA following soil surface applications in the field (Glotfelty et al. 1984). Plastic row covers promote plant growth by maintaining increased temperature, humidity, CO_2, and higher levels of soil moisture (Rickard 1979). Some of these factors are likewise known to influence DCPA dissipation in soils (Glotfelty et al. 1984, Horowitz et al. 1974, Walker 1978). The purpose of this investigation was to determine how the use of several types of plastic row covers influenced residues of DCPA in soils and crops. Broccoli was used as a test crop because of the relatively short interval of time between herbicide application and harvest.

MATERIALS AND METHODS

'Bravo' broccoli was transplanted May 20, 1983 into 3 shallow furrows at 30 x 30 cm spacings on plots measuring 3 x 1 m. The soil was a Berwick loamy sand (Cann et al. 1965) with 4.2% o.m. After transplanting all plots were sprayed with 10 kg/ha DCPA (active ingredient). The plots, except for the uncovered controls, were then covered with one of three types of plastic film that were held in place by covering the margins with soil. The films were: (i) 'ASB' (greenish-yellow tinted with 3.5% perforation provided by 9 mm holes); (ii) 'Xiro' (clear, finely slitted and expandable); and (iii) '3.5% clear' (clear polyethylene with 3.5% perforation provided by 1 cm holes). Prior to covering the plots, thermocouples were inserted into the soil

at a 0.5 cm depth or placed inside styrofoam cups supported 10 cm above the soil surface for the measuring of soil and air temperature, respectively, and these were recorded at 2 hr intervals on selected days by a Campbell Scientific CR5 Digital Recorder. Films were removed at either 15 d ('early removal') or 30 d ('late removal') after transplanting and all plots were harvested June 30, that is 41 d after transplanting. Treatments were replicated three times in a randomized complete block design. Twenty samples of the upper 2.5 cm soil and of 4 random plants from all plots were taken for residue analysis at transplanting, at the two removal dates and at harvest. At harvest, the broccoli sample was separated into the edible 'head' and the discarded 'trim' portion. Samples were stored in polyethylene bags at -10°C until analysis.

Extraction and cleanup of DCPA residues from soil and broccoli employed a modification of the methods of Miller and Gomes (1974) and Zweig(1972), respectively. Briefly, a 20 g sample of air-dried soil was shaken with 100 mL CH_3CN/H_2O (9/1, v/v) for 1 h and then centrifuged. An aliquot equivalent to 5 g soil was added to a 250 mL separatory funnel containing 150 ml 2% Na_2SO_4 solution. The aqueous extract was partitioned twice with 25 mL hexane. The combined hexane phases were dried through Na_2SO_4, diluted to an appropriate volume and injected into the gas chromotograph. With broccoli, a 25 g chopped sample was homogenized for 4 min in a Waring blendor with 75 ml of acetone. The slurry was filtered with suction through a sintered glass funnel and the filter cake was rinsed with acetone. An aliquot of filtrate equivalent to 12.5 g broccoli was added to a separatory funnel containing 150 ml 2% Na_2SO_4 solution and this aqueous solution was partitioned twice with hexane and dehydrated as above. Recoveries were 88.5% and 96.0% for broccoli and soil, respectively.

A MicroTec 220 gas chromatograph equipped with a ^{63}Ni electron capture detector operated in the pulse mode was employed. A 6.1 mm o.d. x 90 cm glass column packed with 3% OV 210 on 100/120 mesh Gas Chrom Q, with an argon/methane carrier gas flow rate of 55 mL/min was used. The inlet, column and detector temperatures were 225, 200 and 280°C, respectively. Under these conditions, DCPA retention time was 1.2 min and 5 x 10^{-2} ng DCPA gave 50% FSD.

Two laboratory studies were conducted to determine (A) DCPA losses in darkness or under UV light from glass, broccoli leaf and soil surfaces; and (B) the effect of the plastic films on DCPA losses in darkness or under UV light. In A, 5 µg DCPA were applied (i) to glass slide coverslips placed in uncovered 4.5 cm dishes, (ii) to a 3.0 cm leaf disk floated on water in a 4.5 cm dish, or (iii) to 1 g pulverized, air-dried soil which was thoroughly mixed and spread as a thin layer in a 4.5 cm dish. These were placed for 16 h in ventillated cabinets either 15 cm under germicidal lamps rated to emit 17 μWcm^{-2} at 1 m at principally 254 nm or in total darkness. The same treatments wrapped in tinfoil were used for controls. DCPA was recovered from the coverslips by shaking for

15 m in 50 mL ethylacetate; from the soil by shaking for 1 h in 50 mL ethylacetate followed by centrifuging; or from the leaf disks by homogenizing in 100 mL ethylacetate followed by centrifuging. Aliquots of each were diluted 50% with hexane and injected without further cleanup. Recoveries exceeded 97%. In this case, a 2 mm I.D x 90 cm glass column packed with 1% DEGS was used with argon/methane carrier gas at 45 mL min^{-1}. Inlet, column and detection temperatures were 200°C, 175°C and 280°C, respectively and DCPA retention time was 0.95 min. In B, 5 µg DCPA were applied to each of four coverslips placed in the bottoms of 9 cm Petri dishes which were then wrapped and sealed with either perforated or unperforated pieces of plastic films. These received the same UV/dark treatments and were extracted in the same manner as A above.

RESULTS AND DISCUSSION

There was little loss of DCPA from the soil until the plastic films were removed (Figure 1). At harvest, DCPA levels in soils were still higher in covered than in the uncovered control plots (Figure 1). The differences in soil residues among plots covered with the three films were not significantly different (data not shown), but levels tended to be lower on 'Xiro' covered plots than on '3.5% clear' covered plots. These results are consistent with a similar trial conducted in 1982 (Jensen and Kimball, unpublished data).

The plastic films also influenced residual levels of DCPA in the crop. Immediately following application, DCPA levels in newly transplanted broccoli were 330 ppm or 1300 µg herbicide per plant (Table 1). At the early plastic removal date, or 15 d after application, uncovered control plants contained 312 µg DCPA per plant or 24% of the initial level. In comparison plants grown under 'Xiro', 'ASB' and '3.5% clear' contained 37, 63 and 68% of the initial level, respectively, at the same date. After being uncovered for 15 d, residue levels were still higher in these previously covered plants than in the uncovered controls. In plants grown under plastic until the late removal date, i.e. for 30 d, 208 to 322 µg DCPA per plant were detected compared to 124 µg in the uncovered control plants. Although the use of plastics significantly prolonged the residual persistence of DCPA in the crop, the levels in the head or edible portion at harvest, were well below the allowable Canadian tolerance of 1.0 ppm. In the trim or waste portion, residues approached this level only in plants grown under plastic until the late removal date (Table 1). Most of these were probably surface residues on the oldest leaves that had been sprayed. There is relatively little foliar uptake, translocation and metabolism of DCPA in plants (Weed Sci. Soc. Amer. 1983).

It has been reported that microorganisms (Hurto et al. 1979, Tweedy et al. 1968) and chemical hydrolysis (Weed Sci. Soc. Amer. 1979) play important roles in DCPA dissipation from soils. Furthermore, breakdown in moist soils is accelerated by

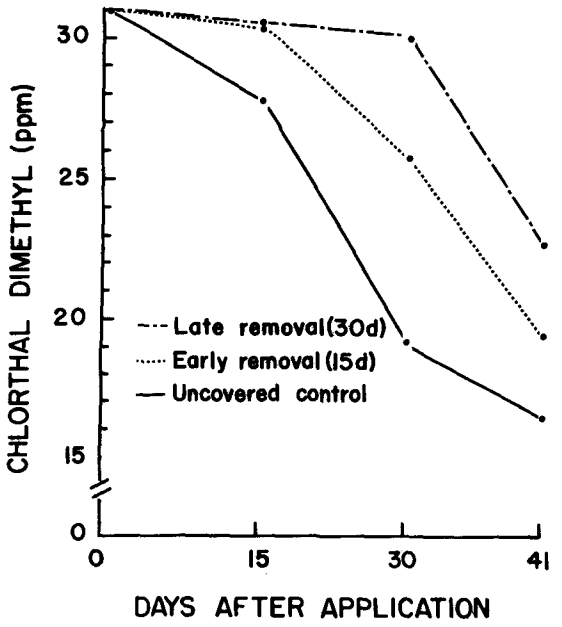

Figure 1. Effect of perforated plastic films and two removal dates on the persistence of DCPA in soil (Means of 3 films).

increasing temperature (Horowitz et al. 1974). Walker (1978) reported that lowering incubation tempertures from 30 to 10°C increased the half-life of DCPA in soil by a factor of 17.9.

In comparison to the uncovered plots, temperature measurements indicated that the plastics, on average, elevated soil temperatures at 0.5 cm and air temperatures at 10 cm by 4.0 and 6.2°C, respectively, on sunny days; by 2.4 and 3.5°C on overcast days; and by 2.5 and 1.3°C at night. However, despite elevating temperatures and maintaining soil moisture which would favor microbial and chemical breakdown, DCPA was more persistent under the plastic films. Subsequent studies demonstrated that measurable levels of DCPA were lost in the dark from dry soil, broccoli leaf and from glass surfaces over a 16 h period (Table 2). Losses from these surfaces were significantly increased under 254 nm UV light, particularly from the leaf surface. DCPA losses from glass coverslips placed in Petri dishes were reduced in both UV light and darkness when the dishes were covered with the plastic films (Table 3). Losses were further reduced when the dishes were covered with pieces of the same films without perforations.

Table 1. Residue levels of DCPA in broccoli grown under various plastic covers with two removal dates*

Type of cover	Removal time	Residue levels (ppm ± s.d.) (µg per plant) At early removal	At late removal	At harvest 'Trim'	At harvest 'Head'
Control* (none)	-	21.03±3.55 (312)	2.05±0.71 (124)	0.24±0.05 (30.2)	0.06±0.06 (3.18)
'Xiro'	early	30.93±1.21 (480)	2.34±0.34 (110)	0.22±0.06 (20.6)	0.40±0.009 (3.11)
	late	**	5.05±0.51 (208)	0.77±0.16 (64.4)	0.048±0.005 (2.54)
'ASB'	early	54.23±11.49 (820)	3.24±0.33 (147)	0.28±0.06 (27.8)	0.052±0.008 (4.16)
	late	**	4.99±1.27 (238)	0.72±0.08 (58.0)	0.043±0.006 (2.86)
'3.5% clear'	early	54.70±8.29 (890)	4.11±0.24 (214)	0.19±0.03 (19.4)	0.039±0.007 (3.34)
	late	**	8.12±1.32 (322)	0.86±0.53 (62.0)	0.059±0.08 (2.78)
S.E.M.		4.233	0.472	0.165	0.0039

*At transplanting, residual levels of DCPA in the treated plant were 327.6 or 1300 µg/plant.
**Assumed to be the same as on early removal date.

Table 2. Levels of DCPA remaining on three surfaces after 16 h under UV (254 nm) or in darkness.

Surface	µg DCPA remaining (+s.d.)[1] UV	Dark
Dry soil	3.18±0.32	4.32±0.51
Leaf	0.26±0.14	3.81±0.29
Glass	2.27±0.44	4.60±0.28
Covered control[2]	5.04±0.23	

[1]S.E.M. = 0.149
[2]Wrapped in tin foil.

These results suggest that DCPA volatility may be a significant factor in its dissipation under field conditions and that it may potentially be photodecomposed. Glotfelty et al. (1984) have recently measured fluxes of DCPA in air above treated soil surfaces and related increasing DCPA flux with increasing soil temperature. Volatility losses required surface moisture. The plastic films would favor vapor losses by elevating temperatures and soil moisture but they would reduce surface air turbulence and trap the DCPA. Vapors escape through the perforations in the films but the plastics per se appear impervious to DCPA (Table 3).

Table 3. Effect of plastic films with and without perforations on loss of DCPA from a glass surface after 16 h in darkness under UV (254 nm) light or in darkness.

Plastic	UV	µg DCPA remaining (±s.d.)[1]	
		UV	Dark
'ASB'	perforated	3.28±0.31	4.35±0.28
	unperforated	3.86±0.23	5.08±0.39
'Xiro'	perforated	3.00±0.36	4.45±0.19
	unperforated	3.22±0.21	4.98±0.35
'3.5% clear'	perforated	3.03±0.31	4.43±0.33
	unperforated	3.78±0.17	5.07±0.25
covered control[2]		5.03±0.28	4.92±0.34
uncovered control		2.82±0.46	4.12±0.40

[1]S.E.M. = 0.144.
[2]Wrapped in tin foil.

Sunlight contains little, if any, of the 254 nm radiation employed in this study so the role of photodecomposition is less clear. However, photodecomposition may occur under field conditions at less energetic wavelengths, possibly catalyzed by light-activated sensitizers (Helling et al. 1971). In this study the films also reduced DCPA losses at 254 nm and may do so at other wavelengths. Regardless, it appears that microbial and chemical degradation are of less importance than volatilization, and possibly photodecomposition when DCPA is applied to and remains at the soil surface. This would account for plastic films increasing DCPA persistence in soils. This increased persistence is not expected to significantly increase residual levels in crops grown for part of the season under plastic.

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