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Volatilization, Off-Site Deposition, and Dissipation of DCPA in the Field

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ABSTRACT

Residues of dimethyl, 2,3,5,6-tetrachloroterephthalate (DCPA) have been found repeatedly in recent years on a variety of produce grown in California to which this herbicide had not been applied. In response to this problem, drift, volatilization, and dissipation of DCPA were investigated in a circular plot seeded with bunch onions [*Allium cepa* (L.) var. White Lisbon], and off-site deposition was measured in a surrounding area seeded with parsley [*Petroselinum crispum* (Mill.) Mansf. var. Green Modified Curl Leaf]. Contamination by residual soil residues remaining on field after harvest was also examined by reseeding the circular plot with parsley. Atmospheric residues detected downwind on resin and filters indicated DCPA moved off-target as a vapor as well as on particles both during and up to 21 d after application. Volatilization flux, measured using the aerodynamic method, reached a maximum rate of 5.6 g ha^{-1}h^{-1}. An estimated 10% of the DCPA applied was lost to the atmosphere within 21 d of application. Deposition of DCPA outside the circular plot was evidenced by residues found on potted parsley plants and soil set out up to 23 m from the treated area. Parsley, seeded around the circular plot at the time of application and sampled 63 d later, contained residues ranging from 51 to 250 µg kg^{-1} indicating DCPA continued to move off-target in air up to 60 d after application. The mass of DCPA in soil exhibited a log-linear decline from which a 50 d dissipation half-life was calculated. Parsley planted in the circular plot after the onion harvest did not contain DCPA residues when sampled 217 and 336 d after the original application. Results indicated that drift during, and volatilization and subsequent atmospheric transport after, application are potentially important sources of DCPA contamination occurring on nontarget crops in California.

T HE California Department of Food and Agriculture (CDFA) routinely analyzes produce samples to ensure they do not contain pesticide residues exceeding established tolerance levels. For the past few years, residues of the herbicide dimethyl 2,3,5,6-tetrachloroterephthalate (DCPA) have been found repeatedly on a variety of produce samples to which it had not been applied. These inadvertent residues generally occur in the coastal growing region of Monterey County and in the central valley in San Joaquin County. From 1984 through 1986 CDFA collected and analyzed 324 parsley (*Petroselinum crispum* Mill.) samples, 16% of which contained residues of DCPA with concentrations ranging from 20 to 310µg kg^{-1} (CDFA, 1984 to 1986). During the same period, DCPA residues were detected on 10, 37, and 11% of the daikon (*Raphanus sativus* L.), dill (*Anethum graveolens* L.), and kohlrabi (*Brassica oleracea* L.) samples, respectively. Because DCPA is not registered for use on

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these crops (Code of Fed. Reg., 1988) tolerance levels have not been established. When residues are found on crops that do not have an established tolerance, the crops are restricted from entering commerce (Gregory, 1987). Due to the occurrence of inadvertent DCPA residues on parsley and other produce, and subsequent economic impact on growers, an investigation into the mechanism of off-target contamination was undertaken.

Pesticide drift during application and subsequent deposition on nontarget crops has long been recognized as a mechanism of off-target movement (Akesson and Yates, 1964). Volatilization after application is also considered a major mechanism of pesticide movement from treated areas (Cliath et al., 1980; Seiber et al., 1986). These two mechanisms are estimated to account for 90% of the pesticide contamination occurring in air (Lewis and Lee, 1976). Therefore, drift during and volatilization after application were considered possible mechanisms of DCPA contamination occurring on produce grown in California.

The relatively long persistence of DCPA in soil might also be a factor contributing to the occurrence of residues on nontarget crops. The half-life of DCPA in soil was estimated to be between 40 and 100 d (Walker, 1978; Hurto et al., 1979), with residues detected up to 12 months after application (Miller et al., 1978). In the coastal and valley regions of California with long growing seasons, parsley and other crops can be rotated every few months. Residues of DCPA found on such produce might result from prior, legal applications transported to plant surfaces via raindrop splash, soil erosion (Pinder and McLeod, 1988), or plant uptake of soil residuals. Therefore, plant uptake and deposition on plant surfaces were also considered in this investigation.

This study was conducted to determine which of the above mechanisms: drift, volatilization (and subsequent deposition downwind), windblown particles, and plant uptake, might be contributing to DCPA contamination of nontarget crops. Drift, volatilization, and dissipation were examined in a circular plot planted with onions (*Allium cepa* L.) surrounded by a crop of parsley. In addition, parsley was rotated into the circular plot 37 d after the onion harvest to determine whether contamination resulted from DCPA residues remaining in soil. The two principal DCPA metabolites, monomethyl 2,3,5,6-tetrachloroterephthalic acid (MTP) and 2,3,5,6-tetrachloroterephthalic acid (TPA), were included in analyses to provide a mass balance accounting of the fate of DCPA in the field.

MATERIALS AND METHODS

Study Site

The study site was a 2.02-ha rectangular field located at the University of California, Davis. This site was selected for two reasons: (i) the plot was isolated from other fields where DCPA use might be occurring, and (ii) this area is

■ Air Samplers
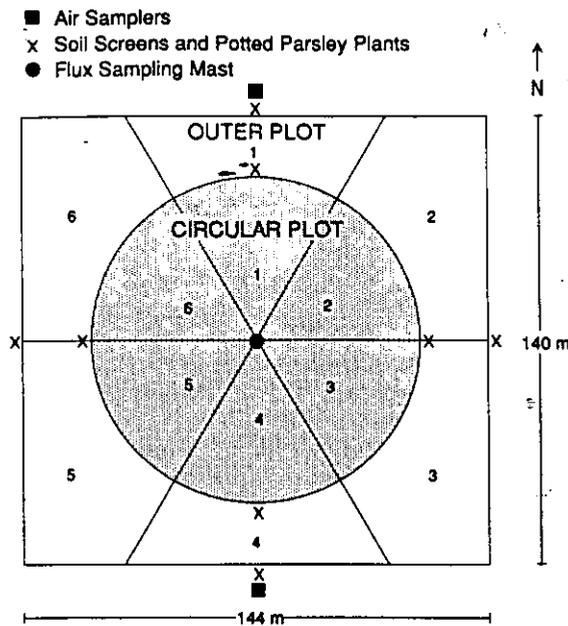✕ Soil Screens and Potted Parsley Plants
● Flux Sampling Mast

Fig. 1. DCPA was applied to the circular plot (radius = 50 m) on 9 Apr. 1987 at a measured rate of 7.08 kg ha⁻¹. Samples were collected from sections (numbered 1–6) in the circular and outer plots.

located in the central valley about 40 km north of the county where inadvertent residues of DCPA have been found. Volatilization flux and soil dissipation of DCPA were measured in a circular plot (50 m radius, Fig. 1). The circular design allowed equidistant monitoring of the movement of DCPA off-site, regardless of wind direction. Soil type was characterized as a Yolo (fine-silty, mixed, nonacid, thermic Typic Xerorthents) with 7 to 8 g kg⁻¹ organic C and 29% sand, 46% silt, and 25% clay (Huntington et al., 1981). Portions of the field had been treated with DCPA in 1982 and 1984, and background soil residues ranged from none detected (detection limit 20 μg kg⁻¹) to 44 μg kg⁻¹.

On 7 and 8 Apr. 1987, onions, a crop with registered DCPA use, were planted (13.5 kg of seed ha⁻¹) in the circular plot. At the same time, parsley, a crop with no registered DCPA use, was planted (5.6 kg of seed ha⁻¹) in the outer plot. Both crops were planted in raised beds 0.61 m apart. A 75% (w/w) wettable powder formulation of DCPA was applied to the circular plot on 9 April at a measured rate of 7.08 kg ha⁻¹ using a tractor-mounted boom sprayer. Pertinent chemical and physical properties of DCPA are listed in Table 1. Onions were harvested on 7 July, 89 d after application. On 13 August (126 d after application), beds in the circular plot were reshaped and reseeded with parsley. On 17 August, the plot was treated with liquid prometryn (1.1 kg ha⁻¹) for additional weed control.

Crops were irrigated with Rain Bird sprinklers operated at a nozzle pressure of 2.76×10^6 Pa, at a rate of 0.43 cm

Table 1. Some chemical and physical properties of DCPA.

Molecular wt.	Solubility†	Vapor‡ pressure	Henry's Law§ constant	K_{oc}¶ (silty loam)
	mg L⁻¹	Pa	atm-m³mol⁻¹	
332	0.5	3.3×10^{-4}	2.2×10^{-6}	3200

† Agrochemicals Handbook, 1983.
‡ DePablo, 1981.
§ Calculated from solubility and vapor pressure.
¶ Brian Korsch, 1988, personal communication, Ricerca, Inc., Painesville, OH.

of water h⁻¹, with an average efficiency of 75%. During the 21-d flux sampling period, irrigation began 24 h after DCPA application and was repeated on Days 3 to 9, 11 to 16, and 18 to 20.

On the day of DCPA application, winds were out of the north with speeds between < 1 and 6.4 m s⁻¹, the daytime high was 29 °C [19% relative humidity (RH)] and low 8 °C (91% RH). Between 10 Apr. and 10 May 1987, winds were predominantly out of the north or south with speeds ranging from 1.0 to 6.9 m s⁻¹. Daytime highs averaged 29 °C and lows 9 °C, with high average RH 85% and low 21%.

Air Sampling

Air samples were collected 30 m upwind and downwind of the circular plot (Fig. 1) on 0 through 5, 8, 11, 14, and 21 d after application to coincide with flux sampling periods (Tables 2 and 3). Air samples were collected using 100 mL of XAD-4 resin (0.84–0.297 mm. 20 to 50 mesh, Rohm and Haas, Philadelphia, PA) preceded by a 20 by 25 cm glass fiber filter in high volume air samplers with flow rates of 1 m³ and min⁻¹. Resin and filters were used to roughly distinguish between vapors and particles, respectively. Upwind concentrations were below the detection limit (0.5 ng m⁻³) indicating external sources of DCPA did not influence results.

Flux samples were drawn through 30 mL of XAD-4 resin in low volume samplers, operating at 50 L min⁻¹. Flux sampling began 10 h after DCPA application and proceeded almost continuously through Day 2 and periodically thereafter (Table 3). Short sampling intervals were used closer to the application date to measure diurnal flux patterns when rates were expected to be at a maximum. Subsequent intervals were longer to estimate an average daytime flux. The aerodynamic method (Parmele et al., 1972), modified by Majewski et al. (1989), was used to calculate atmospheric flux from air concentrations and wind speed data (raw data reported in Ross et al., 1989). Flux samples were collected using a 1.5-m mast located in the center of the circular plot (Fig. 1). Air samples and wind speed measurements were taken 20, 35, 55, 90, and 150 cm above the soil surface. Flux was calculated as the product of concentration and wind gradients, divided by a meteorological stability factor (Majewski et al., 1989).

Off-Target Deposition

Soil screens (consisting of 4 by 10 cm wire mesh covered with a layer of soil) and potted parsley plants were placed

Table 2. Concentrations of DCPA in air 30 m downwind (south) of the circular plot.

Day†	Hour‡	Irrigation§	Concentration, ng m⁻³¶			F/T# ratio
			Resin	Filter	Total	
0	0835–1000		290	420	710	0.59
0	1030–1300		35	150	185	0.81
0	1315–1630		71	48	119	0.40
1	1230–1530	X	910	100	1010	0.10
1	1720–1920	X	260	41	301	0.14
2	1000–1300		150	52	202	0.26
2	1400–1730		22	18	40	0.45
3	1350–1700		47	210	257	0.82
4	1510–1840	X	200	120	320	0.38
8	1035–1535	X	320	24	344	0.07
11	1235–1635	X	61	6	67	0.09
14	1110–1530	X	270	49	319	0.15
21	1014–1415		33	15	48	0.31

† Days after application.
‡ Air sampling interval.
§ An "X" indicates irrigation occurred just prior to air sampling.
¶ Concentrations are an average of two replicate samples except for the sample taken on Day 1 at 1230, which is a single measurement.
# Ratio of filter to total concentration.

in the outer plot at four compass points (N, E, S, and W) and two distances (3 and 23 m) from the edge of the circular plot to assess off-target deposition (Fig. 1). Samples were collected from each site -1, 0, 5, and 10 d after DCPA application.

Soil and Vegetation Sampling

The circular and outer plots were each divided into six sections for soil and vegetation sampling (Fig. 1). Soil samples were collected from the circular plot -1, 0, 1, 7, 14, 21, 42, 63, 84, 168, 217, and 336 d after application from each of the six sections. In each section, four soil plugs (subsamples), 7.6 cm deep, were randomly collected with a stainless steel cylinder (4.13 cm i.d.) and combined into one composite sample. Vegetation samples (100 g) collected in each section consisted of four randomly collected subsamples combined into one composite sample. Onions were collected from the circular plot 42, 63, and 84 d after application. Parsley was collected from the outer plot 63 d after application and from the parsley crop, rotated onto the circular plot, 217 and 336 d after application (91 and 210 d after reseeding).

Chemical Analysis

Air Samples

Resin from high volume samplers was extracted with 150 mL of ethyl acetate by shaking for 30 min. Ethyl acetate was decanted and filtered through Whatman paper no. 1 into a 500-mL round bottom flask. Ethyl acetate (100 mL) was added twice more and swirled for 15 and 10 min, followed by decanting and filtration. Combined extracts were rotoevaporated, transferred to a volumetric flask, and analyzed for DCPA by gas chromatography (GC) using a Hewlett-

Packard (HP) 5730A equipped with a ^{63}Ni electron-capture detector and a 30-m megabore column (J and W Scientific, DB-1). The carrier gas (argon/methane, 90:10 by volume) flow rate was 40 mL min^{-1}. Column, injector, and detector temperatures were 220, 250, and 300 °C, respectively.

Resin from low volume samples was extracted as above with the exception that 50 mL of ethyl acetate was used for all three extractions. Analysis was performed by GC as for high volume samples.

Glass fiber filters were cut into a 125-mL Erlenmeyer flask and extracted with 100-mL methanol plus one drop concentrated HCl. Samples were blended with a Tissuemizer for 1 min. Methanol was decanted and filtered through glass wool into a 250-mL round bottom flask. An additional 50 mL of methanol was added to the Erlenmeyer flask and the sample reblended for 1 min. The solvent was decanted, filtered, and combined, then evaporated to dryness. Samples were quantitatively transferred in ethyl acetate to 15-mL centrifuge tubes and taken to dryness. Diazoethane (3 mL) and 10 μL of 1:3, HCl/ethanol, were added. Samples stood for 15 min then were concentrated with a N evaporator to 0.5 mL. Samples were brought to final volume with ethyl acetate and analyzed for DCPA by GC (HP 5890A) equipped with a mass selective detector operated in selective ion mode, and a 12 m by 0.2 mm methyl silicone column operated in splitless mode. The carrier gas (He) flow rate was 0.68 mL min^{-1}. Injector and transfer line temperatures were 275 and 250 °C, respectively. Column temperature was initially held at 50 °C for 2.5 min, then increased to 250 °C at 30 ;0cC min^{-1} and held for 5 min.

Trapping efficiency of the resin and filter in high volume samplers run for 3 h was determined using 50 μg of DCPA dissolved in 50 μL of ethyl acetate, spiked into a glass tube fitted above the sampling train. Average recovery for the resin plus filter train was 77 ± 11 (n = 3), with an average

Table 3. Calculated flux values plus irrigation, rain, wind speed and air temperature data collected during the 21-d air-sampling period.

Date	Day†	Hour	Flux	Irrigation	Rain	Wind speed‡ 30cm	80cm	Temperature§
			g ha^{-1}h^{-1}	——— cm ———		——— m s^{-1} ———		° C
9 Apr. 1987	0	1845–2045	0.2			0.65	0.90	22
	0	2130–2330	0.05			0.41	0.59	14
10 Apr.	1	0000–0640	0.03			0.58	0.76	10
	1	0930–1210		1.14				
	1	1415–1615	5.1			3.44	4.18	27
	1	1630–1830	2.2			4.50	5.30	21
	1	1900–2100	0.5			2.43	2.95	17
	1	2100–2200			0.02			
11 Apr.	2	0700–0940	3.4			2.19	5.57	11
	2	1000–1300	1.8			6.73	7.16	17
	2	1310–1610	0.09			4.77	5.70	22
	2	1700–2000	0.1			3.21	3.82	20
	2	2030–2330	0.04			1.31	1.71	11
12 Apr.	3	0000–0700	0.1			6.54	7.99	13
	3	0715–1300	0.09			6.63	7.98	19
	3	1330–1530	0.1			4.91	5.85	27
	3	1615–1915		0.89				
13 Apr.	4	1100–1230		0.56				
14 Apr.	5	¶		0.41				
	5	1100–1700	4.2			1.45	1.64	27
17 Apr.	8	¶		0.48				
	8	1045–1400	5.5			4.98	5.85	24
20 Apr.	11	¶		0.56				
	11	1200–1830	2.9			1.38	1.58	29
23 Apr.	14	¶		0.43				
	14	1115–1830	2.8			3.40	3.96	25
30 Apr.	21	0200–0400			0.02			
	21	0930–1630	1.3			5.09	6.03	20

† Day after application.
‡ Wind speeds at 30 and 80 cm calculated from wind profile gradient.
§ Air temperature at 50 cm.
¶ Irrigation occurred just prior to flux sampling.

4.47   0.04   64.6/19= 79.52/19= 376/19 =
3.4   4.2   20

of 86% found on resin. The trapping efficiency of resin in low volume samplers operated for 2 h was determined using 50 µg of DCPA dissolved in 50 µL of ethyl acetate, spiked into a glass tube fitted above the sampler. Resin recovery averaged 95 ± 12 (n = 5).

Soil and Vegetation

Residues of DCPA, MTP, and TPA in 50-g soil samples were extracted with 200 mL acidic acetone (20 ML 5 M H_2SO_4 per 380 mL acetone) by shaking for 2 h. A 50-mL aliquot was treated with 50 mL 0.4 M $NaHCO_3$ and adjusted to pH 10 using 5 M NaOH. The sample was then extracted twice with 50 mL of petroleum ether in a separatory funnel and the aqueous phase set aside. Combined ether extracts were rotoevaporated, dissolved in toluene, reduced to a 5-mL volume on a water bath under a stream of N, and analyzed for DCPA by GC as below.

The aqueous phase solution was adjusted to pH 1 with 10 to 15 mL of 5 M H_2SO_4 and extracted twice with 50 mL 1:1 petroleum ether/diethyl ether. Ether extracts were combined, rotoevaporated, treated with diazopropane to form propylated derivatives of MTP and TPA, dissolved in toluene, and reduced to a 5-mL volume. Samples were then analyzed for MTP and TPA with a Varian 6000 GC equipped with an electron capture detector and a 50-m capillary column (HP, Ultra 1, cross-linked methyl silicone gum) operated at a split ratio of 1:20. The column temperature was initially held at 245 °C for 2 min, then increased at a rate of 2 °C min^{-1} to a final temperature of 265 °C and held for 6 min. Injector and detector temperatures were 250 and 300 °C, respectively.

To estimate soil recovery, 50-g samples of field soil were spiked with 1 to 70 µg of DCPA, MTP, or TPA. Extraction and analysis were conducted as above. Mean recoveries were 91 ± 9 (n = 53), 101 ± 15 (n = 55), and 97 ± 14 (n = 53) for DCPA, MTP, and TPA, respectively.

Residues of DCPA, MTP, and TPA on plant surfaces (dislodgeable residues) were removed by rinsing three times with 100 mL of aqueous Sur-ten solution (2·mL surfactant/98 mL distilled water). Residues of DCPA and some MTP were removed from the Sur-ten solution (ph 5) by adding 40 g of NaCl, shaking for 1 min with 50 mL of methylene chloride in a separatory funnel, and draining the methylene chloride layer through sodium sulfate. This procedure was repeated a total of three times. Remaining MTP and TPA residues were removed from the Sur-ten solution by adding H_2SO_4 to pH 1 and extracting with 1:1 petroleum ether/ethyl ether. Both the methylene chloride and ethyl ether extracts were treated with diazopropane to form derivatized MTP and TPA and analyzed by GC as for soil samples.

To estimate recovery of dislodgeable samples, 50 g of clean vegetation was rinsed with a total of 300 mL aqueous Sur-ten solution as above. The rinsate was then spiked with 2 to 50 µg of DCPA, MTP, or TPA. Mean recoveries for onions were 90 ± 11% (n = 6), 99 ± 1% (n = 2), and 95 ± 15% (n = 5) DCPA, MTP, and TPA, respectively. For parsley these were 91 ± 13% (n = 13), 90 ± 13% (n = 4), and 89 ± 29% (n = 4) for DCPA, MTP, and TPA, respectively.

Internal residues were extracted from foliage (after rinsing with Sur-ten) by mixing with 250 mL of a 1:19 (v/v) mixture of 5 M H_2SO_4/acetone in a high-speed blender. Extraction and analysis were performed as above for soil samples. To determine recovery for internal analyses, 50-g samples of clean vegetation were spiked with 2 to 100 µg of DCPA, MTP, or TPA, following Sur-ten rinse procedures. Mean recoveries for onions were 91 ± 10% (n = 5), 88 ± 13% (n = 4), and 98 ± 12% (n = 4) for DCPA, MTP, and TPA, respectively. For parsley these were 97 ± 12% (n = 14), 101 ± 16% (n = 3), and 98 ± 19% (n = 3) for DCPA, MTP, and TPA, respectively.

RESULTS AND DISCUSSION

Drift and Volatilization

Residues of DCPA were found in downwind air samples on every sampling day (Table 2). Maximum concentrations were detected 1 d after application following the first irrigation. Residues were found on both resin and filter samples (Table 2), indicating DCPA moved off-site in the vapor phase and on particles. The ratio of filter to total concentration (F/T) was generally higher when the plot was dry vs. immediately after irrigation. A Mann Whitney U test (Siegel, 1956) was conducted on the F/T ratio for irrigated and nonirrigated days. A U of 2 was calculated and has a probability of random occurrence of 0.002, indicating that the two groups have significantly different F/T ratios. Thus, the higher F/T ratio on nonirrigated days suggests that soil particles contributed significantly more DCPA residues to the total atmospheric concentration when the field was dry than when wet. Under wet soil conditions, the predominant mechanism of off-target movement appeared to be through the vapor phase. This result is consistent with volatilization flux measurements (see below).

The quantity of DCPA volatilizing from the soil surface vs. the amount lost by soil erosion was not directly sampled in this investigation. The use of resin and filter concentrations in a high volume air sampler, however, is thought to be a reasonable estimate of the vapor/particulate ratio even though it may tend to overestimate the vapor phase (Bidleman, 1988). Using this concept, it was determined that when the field was dry, 26 to 81% of total DCPA was trapped on the filter, representing the particulate portion of DCPA in air. When the field was wet this particulate portion was lower and ranged from 7 to 38% of the total DCPA concentration in air, indicating that 62 to 93% was in the vapor phase. Therefore, the overall contribution of gaseous DCPA to atmospheric concentrations could be substantial since the field was irrigated nearly every day during the first 21 d after application.

Volatilization flux followed the same pattern as downwind air samplers, with higher rates measured after irrigation or rain events (Table 3). Flux rates during the initial three sampling periods were less than 0.2 g ha^{-1}h^{-1}. These samples were collected to 10 h after application and prior to the first field irrigation. After the first irrigation on Day 1, rates increased to 5.1 g ha^{-1}h^{-1} and subsequently decreased during the afternoon as the field dried out. During the evening, 0.02 cm of rain fell and subsequent flux measurements again increased, with a decline in rates seen as the field dried out. The dependence of flux on soil moisture has been observed in prior studies (Spencer and Cliath, 1973; Taylor et al., 1977) even for nonincorporated pesticides residing in a thin layer at the soil surface (Glotfelty et al., 1984). In addition, the correlation between irrigation events and high flux rates indicates that flux is predominantly a measure of volatilization from the field since under wet soil conditions particulate loss would be at a minimum.

The maximum flux rate was 5.6 g ha^{-1}h^{-1}, close to the maximum found for DCPA by Glotfelty et al. (1984) of 8 g ha^{-1}h^{-1} in a Maryland field study. Ex-

trapolating over 21 d after application by averaging data points around missing values, an estimated 700 g ha^{-1} of DCPA was lost during daylight hours as a result of flux alone, or about 10% of the total applied. This is a rough estimate because flux determinations were only made on 9 of 21 d.

Off-Target Deposition

During application, both soil screens and potted parsley plants contained DCPA residues at 3 and 23 m from the circular plot (Table 4). Residues were higher in the southern direction, which corresponded to the predominant wind patterns during application. After DCPA application, new soil screens and potted parsley were placed at the same locations and residues were observed on them, which also correlated in magnitude with prevailing winds (i.e., north–south direction). The total mass deposited off-target from 5 through 10 d after application was 3.9 g ha^{-1}, calculated from soil screen residues. Deposition of DCPA off-target could be through dry deposition of particles as well as by adsorption of vapors by soil (Smith, 1981). Extrapolating to a 21-d period (assuming a constant deposition rate), then adding the mass found on the day of application, an estimated 17 g ha^{-1} was deposited within a 23-m radius of the application site. This mass is small compared with the flux mass of 700 g ha^{-1} and indicates only 2% of the DCPA fluxing from the circular plot within 21 d of application deposited within 23 m. The remaining 98% might undergo long-range transport as vapor or attached on small particles, and subsequently deposit further off-target via dry deposition or rain-out. Long-range transport of a variety of pesticides is well documented in the literature (Cohen and Pinkerton, 1966; Risebrough et al., 1968; Lewis and Lee, 1976).

Residues of DCPA were found in both dislodgeable and internal fractions of potted parsley samples on the day of application (Table 4). Because background samples did not contain DCPA, these results indicated that either parsley rapidly absorbed DCPA through the stomata, or washing with Sur-ten solution did not completely remove all surface deposits. It was not clear whether internal and dislodgeable residues were adequately separated, therefore both residues were combined in Table 4 for discussion purposes.

Nine of the 24 DCPA concentrations found on potted parsley in this study (Table 4) were higher than illegal residues reported on parsley in California from 1984 to 1986 (CDFA, 1984–1986). The rest were less than 310 μg kg^{-1}, the maximum concentration found by CDFA during routine monitoring, indicating parsley planted within 23 m of a legal application of DCPA could easily contain similar DCPA residues. This contamination could occur by simple spray drift (as seen for soil screens and potted parsley exposed on Day 0), and by postapplication drift of DCPA (as seen for soil screens and potted parsley collected 5 and 10 d after application). In addition, because about 98% of the DCPA lost to the atmosphere did not deposit within 23 m of the circular plot, it is possible a portion of these airborne residues could deposit on nontarget crops further downwind.

Soil Residues

Three of the eight background samples contained small amounts of DCPA (44 μg kg^{-1} or less) as this material had been applied to a portion of the plot 3 yr earlier. Persistence of DCPA 1 yr after application was reported previously (Miller et al., 1978) with indications that at cool temperatures (10 °C) degradation does not occur within 90 d. Cool temperatures exist in this region of California in winter, slowing degradation of DCPA, and perhaps account for the residues found in background samples. None of the background samples contained detectable levels of either degradation product.

Concentrations of DCPA ranged from an average 5800 μg kg^{-1} on the day of application to 120 μg kg^{-1} 336 d after treatment (Table 5). Degradation of DCPA occurs by hydrolysis of the ester linkages forming MTP and TPA (Gershon and McClure, 1966). Degradation in soil was reported to be primarily via microbial activity with the possibility of simple chemical degradation contributing as well (Hurto et al., 1979; Tweedy et al., 1968).

Concentrations of MTP rose slightly 63 d after application and then declined afterward (Table 5). A

Table 4. Concentrations of DCPA on soil screens and potted parsley plants at four compass points and two distances from the circular plot.

		North		East		South		West	
	Day†	3 m	23 m	3 m	23 m	3 m	23 m	3 m	23 m
Soil screen		ng cm^{-2}, dry wt.							
	−1	ND‡	ND	ND	ND	ND	ND	ND	ND
	0	5	3	9	6	43	9	2	3
	0–5	−§	—	—	—	—	—	—	—
	5–10	120	35	21	53	56	59	9	4
Potted parsley		μg kg^{-1}, fresh wt.							
	−1	ND	ND	ND	ND	ND	ND	ND	ND
	0	3	ND	260	ND	14 000¶	1 200	ND	3
	0–5	430	87	180	62	600	170	140	24
	0–10	1100	380	620	160	2 500	640	210	58

† Days after application. After DCPA was applied on Day 0, new soil screens and potted parsley plants were placed around the field after application and collected 5 and 10 d later (0–5 and 0–10, respectively). However, due to rain, soil screens were replaced on Day 5 and collected 5 d later (5–10).
‡ None detected. Detection limit was 0.2 μg per sample.
§ Sample lost due to rain on Day 1.
¶ Sample may have been sprayed directly or otherwise contaminated.

Table 5. Mean concentrations of DCPA, MTP, and TPA in soil and vegetation of the circular plot.

Day†	Soil‡			Vegetation§		
	DCPA	MTP	TPA	DCPA	MTP	TPA
			μg kg⁻¹			
-1	12 (21)¶	ND#	ND	$-$††	$-$	$-$
0	5800 (1900)	28 (10)	ND	$-$	$-$	$-$
1	7000 (620)	21 (10)	ND	$-$	$-$	$-$
7	5600 (1400)	35 (5)	4 (5)	$-$	$-$	$-$
14	5600 (1300)	38 (9)	23 (12)	$-$	$-$	$-$
21	4100 (1400)	84 (66)	490 (790)	$-$	$-$	$-$
42	2900 (1600)	31 (17)	920 (330)	620 (280)	33 (14)	64 (29)
63	1800 (710)	98 (22)	810 (350)	220 (57)	14 (11)	42 (26)
84	1100 (480)	15 (18)	710 (480)	120 (54)	31 (6)	44 (18)
168	110 (57)	ND	120 (76)	$-$	$-$	$-$
217	220 (71)	ND	53 (42)	ND	ND	ND
336	120 (29)	ND	22 (17)	ND	ND	ND

† Days after application.
‡ Soil concentrations expressed in dry wt.
§ Vegetation concentrations expressed in fresh wt. Onions were sampled 42, 63, and 84 d after application while parsley was sampled 217 and 336 d after application.
¶ Mean of six replicates with standard deviation in parentheses.
\# None detected. Detection limit was 20 μg kg⁻¹ for all three compounds in soil and vegetation.
†† Sample not taken.

steady increase in MTP was seen by Hurto et al. (1979) in a laboratory study conducted over 112 d. Concentrations of MTP in the field, however, did not exhibit this trend, perhaps due to the subsequent formation of TPA, a process that was not observed in the laboratory (Hurto et al., 1979).

Initially, TPA residues were low or not detected, followed by a slight increase as DCPA degraded to MTP, with a subsequent decline toward the end of the study (Table 5). Iyer et al. (1969) saw a similar trend for these degradation products in a laboratory study. The higher concentrations of TPA, as compared with MTP, and its persistence in soil beyond the time when MTP residues were no longer detected, suggests it is more persistent than MTP.

Vegetation Residues

Mean concentrations of DCPA in and on onions ranged from 620 μg kg⁻¹ at initial sampling to 120 μg kg⁻¹ at harvest (Table 5), well below the tolerance level of 1000 μg kg⁻¹ (Code of Fed. Reg., 1987). Whether residues resulted from plant uptake of soil residues, or from atmospheric deposition on the onion foliage could not be determined from these data. Plant uptake of DCPA, however, has been implied in studies conducted with carrot (*Daucus carota* L.), radish (*Raphanus sativus* L.) pine (*Pinus* sp.) seedlings (Gilbert and Lisk, 1978; Archer and Gauer, 1980; Iyer et al., 1969;) indicating DCPA might be taken up systematically by certain species.

Parsley planted outside the onion plot also contained DCPA residues when sampled 63 d after application (64 d after seeding). Concentrations were 250, 80, 40, 72, 51, and 140 μg kg⁻¹ in Sections 1 through 6 of the outer plot, respectively. These residues resulted from aerial transport of DCPA from the circular plot. Detection of DCPA on plants in the outer plot indicated parsley seeded at the time of DCPA application can contain residues similar to those found by CDFA in routine monitoring, even though plants had emerged about 30 d after application.

Parsley planted back in the circular plot immediately after onion harvest did not contain detectable residues of DCPA when sampled 217 and 336 d after application (Table 5). It is conceivable parsley plants did contain DCPA residues, but at concentrations below the detection limit of 20 μg kg⁻¹. For example, residues found on onions were approximately an order of magnitude lower than soil residues. When parsley was sampled from the circular plot, soil concentrations were 120 to 220 μg kg⁻¹. An order of magnitude lower would put plant residues at or below the detection limit. Nevertheless, these data indicate rotating parsley onto DCPA treated fields 126 d after application does not cause detectable DCPA residues and is therefore not a mechanism of off-site contamination under these conditions.

Mass Balance Budget

The mass of DCPA recovered in the treated onion plot declined exponentially with time (Table 6). A 50-d dissipation half-life was calculated for this silty-loam soil, which is in close agreement with Walker's (1978) laboratory half-life of 40.5 d. Leaching was not found to be a significant mechanism of DCPA dissipation from soil (data not shown, see Ross et al., 1989). Volatilization was, however, accounting for 29% of the DCPA lost from soil (i.e., 2380 g ha⁻¹ lost to the atmosphere as measured by flux). The large percentage of mass lost to the atmosphere indicates the half-life calculated for DCPA is not a degradation half-life, driven solely by a first-order decay process. In addition r^2 for the log-linear model was 0.86, leaving about 14% of the variability in reduction of DCPA mass over time, unexplained by the model. Because dissipation processes, such as volatilization, are not necessarily log-linear, the inability of this simplistic model to account for all variability is understandable.

Residues of MTP in the field on any given sampling date accounted for 1%, or less, or the total DCPA applied (Table 6). Residues of TPA were generally higher than MTP and on any given sampling date accounted

Table 6. Mass of DCPA, MTP, and TPA recovered in air, soil, and vegetation of the circular plot. A total of 7.08 kg ha⁻¹ was applied on 9 Apr., 1987.

	Air‡	Soil§			Vegetation§,¶			% of applied
Day†	DCPA	DCPA	MTP	TPA	DCPA	MTP	TPA	
				— kg ha⁻¹ —				
0	1.3×10^{-3}	5.89	0.028	ND#	—††	—	—	84
1	0.012	6.04	0.019	ND	—	—	—	86
7	0.032	4.69	0.029	2.8×10^{-3}	—	—	—	67
14	0.027	4.77	0.031	0.019	—	—	—	68
21	0.012	3.51	0.070	0.42	—	—	—	57
42	—	2.71	0.029	0.84	7.8×10^{-4}	4.1×10^{-5}	7.9×10^{-5}	51
63	—	1.61	0.086	0.71	1.9×10^{-3}	1.1×10^{-4}	3.7×10^{-4}	34
84	—	1.03	0.014	0.65	6.2×10^{-3}	1.7×10^{-3}	2.4×10^{-3}	24
168	—	0.09	ND	0.10	—	—	—	3
217	—	0.19	ND	0.05	ND	ND	ND	3
336	—	0.11	ND	0.02	ND	ND	ND	2

ln(DCPA mass, kg ha⁻¹, in soil) = 1.48 − 0.0138 (day) $R = 0.86$

† Days after application.
‡ Data extrapolated to a 12-h period on Days 7, 14, and 21.
§ Mean of six replicates.
¶ Onions were sampled 42, 63, and 84 d and parsley on 217 and 336 d after application.
# None detected. Detection limit was 20 μg kg⁻¹ for all three compounds in soil and vegetation.
†† Not sampled.

for as much as 12% of the mass applied. These data suggest that MTP is less stable in the soil environment than TPA.

Residues of DCPA and the two degradation products in vegetation taken from within the circular plot were less than 1% of the total mass applied. This is consistent with other research on pine seedlings using ¹⁴C-labeled DCPA (Iyer et al., 1969).

CONCLUSIONS

Off-target movement of DCPA in air occurred both during and after pesticide application. The highest concentrations in air downwind of the circular plot occurred 1 d after application when the field was first irrigated. Downwind air samples indicated that DCPA moved off-target as a gas and on particles both during and after application. Deposition of DCPA occurred off-site both during and after application as evidenced by residues found on soil screens and potted parsley placed up to 23 m outside the circular plot.

From this research it was not possible to directly quantify the contribution of gaseous and particulate bound DCPA to total atmospheric residues. Estimates from filter and resin residues, however, indicate that when the field was wet, 62 to 93% of atmospheric residues were in the vapor phase. Because the field was irrigated almost daily, vapor movement could be an important mechanism of off-site contamination.

Results indicate the primary mechanism of DCPA contamination in adjacent plots is from atmospheric transport both during and after application. An estimated 10% of the total DCPA applied was lost to the atmosphere over a 21-d period. Approximately 2% of the total DCPA lost by this process was deposited within 23 m of the circular plot. The remaining 98% was therefore available for further transport, The effectiveness of buffer zones as a means of controlling off-site deposition, however, could not be determined from this investigation because samples were not taken beyond 23 m of the treated area.

In addition, parsley planted back onto the circular plot within 126 d of application did not contain de-

tectable residues, even though soil samples still contained small amounts of DCPA. Thus rotation of parsley onto fields previously treated with DCPA did not lead to contamination under these small plot conditions.

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REFERENCES

Agrochemicals Handbook. 1983. Royal Society of Chemistry, The Univ. of Nottingham, England.

Akesson, N.B., and W.E. Yates. 1964. Problems relating to application of agricultural chemicals and resulting drift residues. Ann. Rev. Entomol. 9:285–318.

Archer, T.E., and W.O. Gauer. 1980. Levels of DCPA, MTP, TPA, and hexachlorobenzene in radish roots and tops. HortSci. 15:146–147.

Bidleman, T.F. 1988. Atmospheric processes. Environ. Sci. Technol. 22:361–367.

California Department of Food and Agriculture. 1984–1986. Pesticide use enforcement. Chemical Residues Rep. CDFA, Sacramento, CA.

Cliath, M.M., W.F. Spencer, W.J. Farmer, T.D. Shoup. and R. Grover. 1980. Volatilization of S-ethyl N, N-dipropylthiocarbamate from water and wet soil during and after flood irrigation of an alfalfa field. J. Agric. Food Chem. 28:610–613.

Code of Federal Regulations. 1988. Tolerances and exemptions from tolerances for pesticide chemicals in or on raw commodities. In Protection of Environment. 40CFR, Chapter 1, Part 180. p. 357. The Office of the Federal Registrar, National Archives and Records Administration, Washington, DC.

Cohen, J.M., and C. Pinkerton. 1966. Widespread translocation of pesticides by air transport and rain-out. In R.F. Gould (ed.) Organic pesticides in the environment. Adv. Chem. Ser. no. 60. Am. Chem. Soc., Washington, DC.

DePablo, R.S. 1981. Vapor pressure of dimethyl tetrachloroterephthalate. J. Chem. Eng. Data 26:237–239.

Gershon, H., and G. McClure, Jr. 1966. Approach to the study of the degradation of dimethyl tetrachloroterephthalate. Contrib. Boyce Thompson Inst. 23:291–294.

Gilbert, M., and D.J. Lisk. 1978. Residues of dacthal herbicide in carrots. Bull. Environ. Contam. Toxicol. 20:180–183.

Glotfelty, D.E., A.W. Taylor, B.C. Turner, and W.H. Zoller. 1984. Volatilization of surface-applied pesticides from fallow soil. J.

Agric. Food Chem. 32:638–643.

Gregory, B.M. 1987. Produce carrying spray residue: Violations. p. 249–250. *In* Food and agricultural code. State of California, Dep. of Food and Agric., Supply Services, Sacramento, CA.

Huntington, G.L., J.C. Wardlaw, M. Minno, W. Allardice, C. Monti, and A. Shen. 1981. The soil survey of the University of California, Davis. Dep. of Land, Air and Water Resour., Davis, CA.

Hurto, K.A., A.J. Turgeon, and M.A. Cole. 1979. Degradation of benefin and DCPA in thatch and soil from a Kentucky bluegrass (*Poa pratensis*) turf. Weed Sci. 27(2):154–157.

Iyer, J.G., G. Chesters, and S.A. Wilde. 1969. Chlorthal degradation in soils and its uptake by pine seedlings. Weed Res. 9:53–61.

Lewis, R.G., and R.E. Lee, Jr. 1976. Air pollution from pesticides: Sources, occurrence, and dispersion. p. 5–50. *In* (ed.) Air pollution from pesticides and agricultural processes. R.E. Lee, Jr. CRC Press, Inc., Boca Raton, FL. Drift + volatilization

Majewski, M.S., D.E. Glotfelty, and J.N. Seiber. 1989. A comparison of the aerodynamic and the theoretical-profile-shape methods for measuring pesticide evaporation from soil. Atmos. Environ. 23:929–938.

Miller, J.H., P.E. Keeley, R.J. Thullen, and C.H. Carter. 1978. Persistence and movement of ten herbicides in soil. Weed Sci. 26(1):20–27.

Parmele, L.H., E.R. Lemon, and A.W. Taylor. 1972. Micrometeorological measurements of pesticide vapor flux from bare soil and corn under field conditions. Water Air Soil Pollut. 1:433–451.

Pinder, J.E., III, and K.W. McLeod. 1988. Contaminant transport in agroecosystems through retention of soil particles on plant surfaces. J. Environ. Qual. 17:602–607.

Risebrough, R.W., R.J. Hugget, H.J. Griffin, and E.D. Goldsberg. 1968. Pesticides: Transatlantic movements in the northeast trades. Science (Washington, DC) 159:1233–1236.

Ross, L.J., S. Nicosia, K.L. Hefner, D.A. Gonzalez, M.M. McChesney, and J.N. Seiber. 1989. Volatilization, off-site deposition dissipation and leaching of DCPA in the field. California Dep. of Food and Agric. Rep. EH89-2. CDFA, Sacramento, CA.

Seiber, J.N., M.M. McChesney, P.F. Sanders, and J.E. Woodrow. 1986. Models for assessing volatilization of herbicides applied to flooded rice fields. Chemosphere 15:127–138. Volatilization

Siegel, S. 1956. Non parametric statistics. McGraw Hill Book Co., New York.

Smith, W.H. 1981. Air pollution and forests. Springer-Verlag, New York.

Spencer, W.F., and M.M. Cliath. 1973. Pesticide volatilization as related to water loss from soil. J. Environ. Qual. 2:284–289.

Taylor, A.W., D.E. Glotfelty, B.C. Turner, R.E. Silver, H.P. Freeman, and A. Weiss. 1977. Volatilization of dieldrin and heptachlor residues from field vegetation. J. Agric. Food Chem. 25:542–548.

Tweedy, B.G., N. Turner, and M. Achituv. 1968. The interactions of soil-borne microorganisms and DCPA. Weed Sci. 16:470–473.

Walker, A. 1978. Simulation of the persistence of eight soil-applied herbicides. Weed Res. 18:305–313.

Microbial Transformation of 1,2-Dibromo-3-Chloropropane (DBCP)

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ABSTRACT

A once widely used nematicide that is now banned, 1,2-dibromo-3-chloropropane (DBCP), persists in groundwaters and is a significant pollutant in some water supplies. A study was conducted to determine whether a means for the biodegradation of this persistent compound could be devised. DBCP was not converted to organic products, halide, or CO_2 in unamended samples of soil, subsoil material, or groundwaters in 60 d, and no microorganism could be isolated that was able to use the compound as a C source for growth. However, cell suspensions of *Pseudomonas putida* and of bacteria grown in solutions containing chlorinated fatty acids or 3-chloro-1-propanol cometabolized DBCP in the presence of O_2 with the formation of halide but not CO_2. *Pseudomonas putida* had the greatest activity. DBCP was also converted aerobically to organic products and CO_2 by soil suspensions incubated with methane. The compound was also converted anaerobically to organic products but not CO_2 in suspensions of soil, but no anaerobic transformation was observed in samples of groundwater or aquifer solids. We suggest that biological treatment may be used as a means to destroy this pollutant.

T HE NEMATICIDE 1,2-dibromo-3-chloropropane (DBCP) persists in areas in which it was used as a pesticide. In California, DBCP is a frequent contaminant in wells, the concentrations usually ranging between 0.1 and 9.9 μg/L (Cardoza et al., 1985; Peoples et al., 1980). Similarly, DBCP at concentrations of 0.02 to 20 μg/L has been detected in groundwaters in Hawaii, Arizona, South Carolina, and Maryland (Cohen

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et al., 1984). Although this nematicide has been banned for most uses since 1978 because of evidence of human toxicity (USEPA, 1977), its presence in potable waters at concentrations that exceed regulatory standards poses a risk to human health. In addition to its presence in aquifers below or near fields where it was used to control nematodes, the compound is still being detected at sites near which it was manufactured, and the costs for remediation of the area are estimated to be exceedingly high (Shabecoff, 1988).

The loss of DBCP from soils by volatilization after field applications can be substantial (Saltzman and Kliger, 1979), but once the chemical reaches deeper soil horizons and groundwaters, the loss by volatilization is probably not significant (Hodges and Lear, 1974). The compound appears to be resistant to abiotic degradation, and the half-life of DBCP under conditions prevailing in many groundwaters of the USA is estimated to exceed 114 yr (Burlinson et al., 1982). On the other hand, some evidence exists that DBCP may be subject to microbial transformation. Thus, Castro and Belser (1968) demonstrated reductive dehalogenation of DBCP in soil suspensions supplemented with glycerol, although they could not isolate a pure culture or demonstrate dehalogenase activity in the absence of soil. Nongrowing cultures of *Pseudomonas putida* (Lam and Vilker, 1987) and a strain of *Flavobacterium* (Castro and Bartnicki, 1968) have been shown to dehalogenate DBCP.

Because of the widespread occurrence of groundwaters contaminated with the compound, its threat to health, and the high cost of site remediation, a study was undertaken to determine factors that control the microbial transformation of DBCP. This information should prove useful in devising a field technology to