FINAL REPORT

CONTRACT #7820

Volatilization Rate and Downwind Contamination From Application of Dacthal Herbicide to an Onion Field

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ABSTRACT

This is a summary report for a 1987 field project conducted at UC Davis to determine the volatilization rates (flux) of dacthal (DCPA, dimethyl 2,3,5,6-tetrachloroterephthalate) and two of its transformation products, monomethyl 2,3,5,6-tetra-chloroterephthalic acid and 2,3,5,6-tetrachloroterephthalic acid, from soil. Air samples, downwind and upwind high volume and low volume in the center of the field, and soil screen samples were taken from April 9 through April 30, 1987 for analysis. Vertical flux was determined from low volume air samples and micrometeorological data using the Thornthwaite-Holzman (TH) and Theoretical-Profile-Shape (TPS) methods of calculation.

Determination of volatilization flux by the aerodynamic method led to an estimated volatilization flux of 101.1 g/plot (TH method) and 135.1 g/plot (TPS method) during the measurement periods following application. When compared with the amount of dacthal lost from the soil by all processes during the 21 day period, these values represent 5 and 7%, respectively, of the total lost. When account is taken of daylight periods when no flux measurements were conducted, extrapolation leads to a loss by volatilization of 27-33% of the total dacthal lost from the soil by all processes.

All of the chemical detected in air samples and soil screen samples was as the parent product. Only the CDFA split soil core samples gave results higher than the limit of detection for the transformation products.

INTRODUCTION

Residues of dacthal (DCPA) herbicide were detected in 86 samples of a variety of crops for which there was no registered use in the period 1981 to 1985 (CDFA). Most of these samples were of vegetables grown in Monterey County and, although the residue levels were usually quite low, they were technically illegal and thus prevented these crops from entering commerce. Of the 86, 27 were caused by illegal applications or contamination of equipment used in the process of application. The remaining 59 were believed to be caused by drift or other airborne movement, but the patterns of contamination were frequently not such to allow a definite assignment of them to simple spray drift. In response to this problem, CDFA's Environmental Hazard Assessment Program (EHAP) established a field test at UC Davis in an attempt to define the rates and mechanisms of dacthal dissipation from an experimental plot. The EHAP test was designed to provide a material balance within the field and also assess off-target movement. The off-target movement by volatilization and deposition was measured by UC Davis collaborators, and is the subject of this report.

OBJECTIVES OF PROJECT

1. Measure the volatilization rate (flux) of dacthal and two of its transformation products from a treated field planted with onions.

2. Analyze for off-target transport using high volume air samplers, soil-coated screen samples, and mature parsley plants placed just outside the treated field.

EXPERIMENTAL

Field Study

A circle was inscribed within a 5.12 acre rectangular area (Figure 1.) located just to the west of the main UC Davis Campus at the Land, Air and Water Resources field area. Fertilizer, (34-0-0) at 139 lbs nitrogen/acre, was applied in 7.62 m passes with a Vicon broadcast fertilizer rig on April 2, 1987. The field was bedded up with 1.016 m rows 35.6 cm apart, the rectangular area was marked and the circle was approximated using rectangular strips in the following manner:

The center of the rectangle was determined and a center line 100 m in length was marked off. Small rectangular strips consisting of three beds wide (3.04 m) were measured from the center line and staked at each boundary end (Figure 2). The sum of the inscribed rectangular strips was approximately 0.55% greater in area than a 50 m radius circle. The circular area was planted with 20.6 lbs of white lisbon onion seed on April 6 through April 8, 1987. Planting was accomplished with Planet Junior Sled and scatter shoe. Seeds were sown 3.2 to 6.4 mm deep in 5.08 cm wide bands. Forest green parsley was planted inside the perimeter of the rectangle but outside the perimeter of the circle using the same procedures used for onions. Dacthal®, 75 W wetable powder, was applied at a theoretical rate of 11.2 kg/ha to the 0.79 ha circular plot on April 9,1987.

Table 1 gives the activity schedule for the project. Table 2 lists the equipment and materials used.

Meteorological Instrumentation

Four rotating cup anemometers were attached to a 2.54 cm X 1.5 m pole located in the center of the circle. The anemometer heights were adjusted in a logarithmic pattern from the soil surface. The anemometers were calibrated prior to field experimentation, by positioning all on a horizontal line directly into the wind, thereby minimizing the influence of one anemometer on the other. Located next to the meteorological mast was a shielded and aspirated ten junction thermopile that measured differential air temperature (del T). The height of each tube was 30 cm (z_1) and 80 cm (z_2); these heights determined the flux plane[1] at 50 cm. The measurement accuracy of the thermopile was 0.02 °C. A wind direction vane was also located in the center of the field. Cables from the meteorological instrumentation extended north along a furrow to just outside the treated circle to a datalogger.

1 The flux plane is determined by the geometric equation: $Z = (Z_1 Z_2)^{1/2}$

The meteorological data was collected every three seconds, and summed and averaged over 15 minute periods. These 15 minute averages were downloaded in the laboratory into an IBM PC via a tape recorder each sampling day. Further data reduction was done utilizing Lotus 1-2-3.

Figure 1. Field Diagram

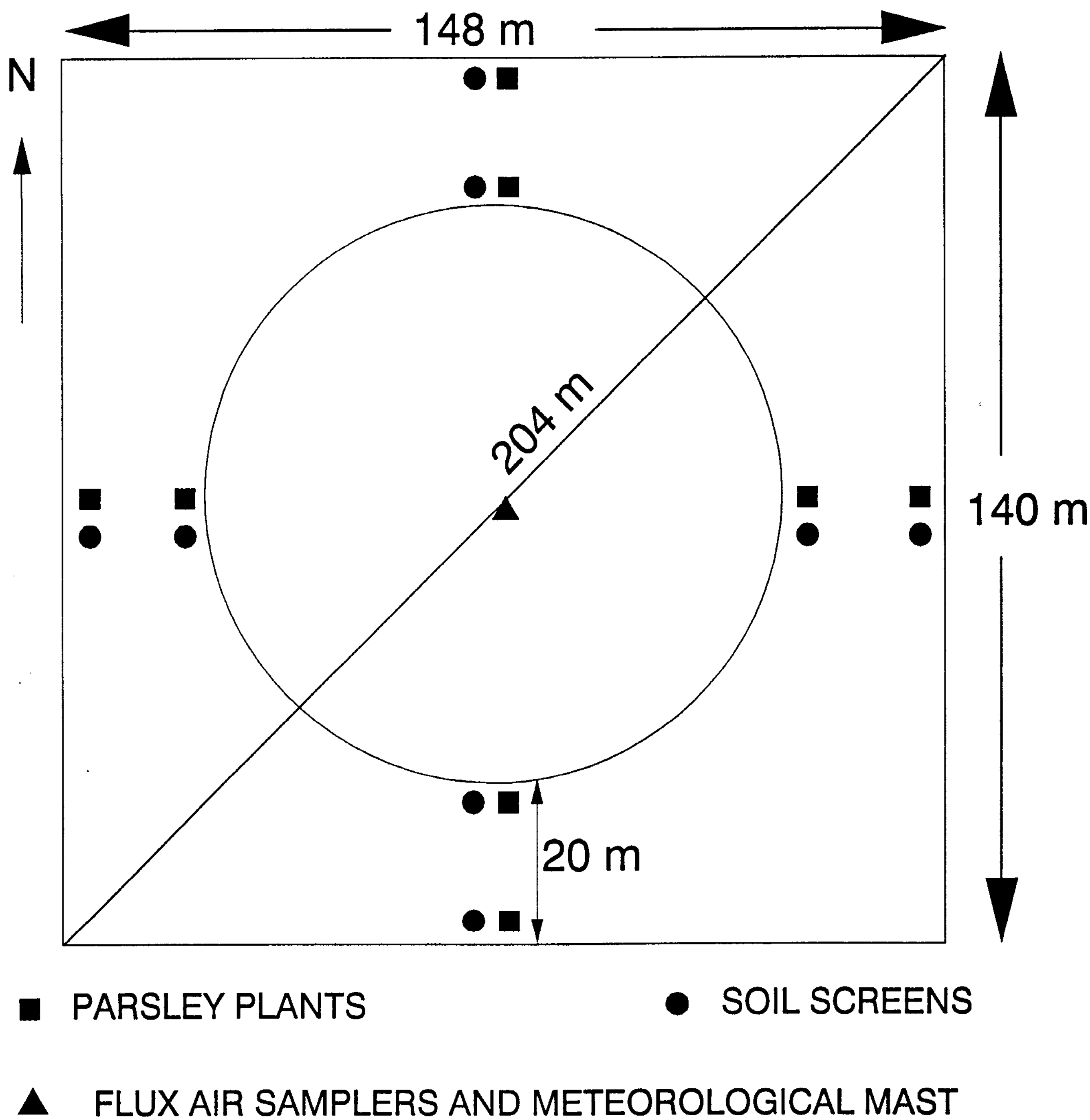

Figure 2. Circular Plot Estimation

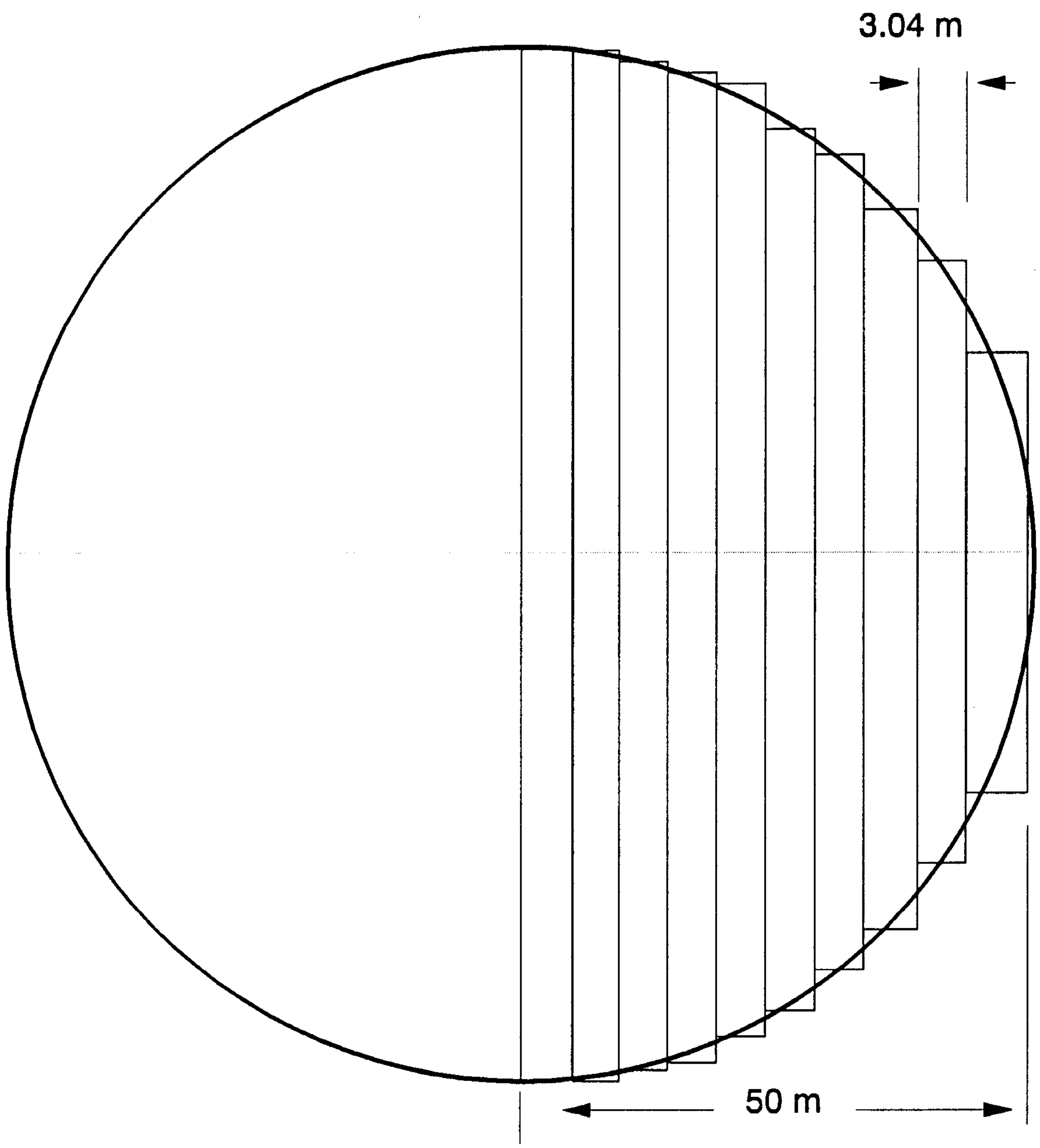

Table 1. List of Events.

Date	Activity
4/2/87	Fertilized with 139 pound of nitrogen/acre (34-0-0).
4/2/87	Field bedded up.
4/5/87	Circular plot laid out.
4/5/87	Background soil screens set in place.
4/7/87	Background soil screens collected.
4/6/87-4/8-87	Onion and parsley planted.
4/9/87	Dacthal® 75 W applied at 10 pounds/acre. Irrigation pipe set out.
4/9/87	High volume air samples taken during and after dacthal application. Soils screens set out after application was completed. Flux sampling begun at 19:00.
4/10/87	Flux sampling from 00:00 to 07:00. Field irrigated for 2.6 hr. Flux sampling resumed at 1400. Downwind high volume air sampling. Soil screens picked up and a new set placed in position. Flux sampling terminated when rain began to fall at 21:00.
4/11/87	Downwind air sampling. Two hour flux sampling period beginning at 07:00 until 15:30.
4/12/87	Flux sampling. Downwind air samples. Field irrigated for 1.3 hours prior to flux sampling.
4/13/87	Flux sampling. Downwind air samples. Field irrigated for 1.3 hours prior to flux sampling.
4/14/87	Day 5 flux sampling. Downwind air samples. Field irrigated for 0.9 hours prior to flux sampling. New soil screens set in place.
4/17/87	Day 8 flux sampling. Downwind air samples. Field irrigated for 1.1 hours prior to sampling.
4/19/87	Soil screens retrieved.
4/20/87	Day 11 flux sampling. Downwind air samples. Field irrigated for 0.7 hours prior to sampling.
4/23/87	14 day flux sampling. Downwind air samples. Field irrigated for 1.0 hours prior to flux sampling.
4/30/87	21 day flux sampling. Downwind air samples. No irrigation.
7/6/87	Soil screens laid out. Duplicate downwind high volume air samples taken. Onions harvested by hand.
7/7/87	Harvesting of onions continued. Soil screens collected.

Table 2. List of Equipment and Materials Used.

1.	Wind Profile Register System, Model 104-LED-LM-DC CWT-1791, Thornthwaite and Associates, Elmer, NJ.
2.	Microdatalogger Mode[1]. CR-21X Campbell Scientific, Logan UT.
3.	High volume air samplers, Model U-1/AT, BGI Inc., Waltham, MA.
4.	Generators, Honda Motor Co.
5.	Ten junction thermopile for measuring change in temperature, D.E. Glotfelty.
6.	Glass fiber filters, 4.25 cm dia., #934-AH Whatman, Clifton, NJ (flux samples).
7.	Glass fiber filters 8 X 10 for high volume sampling.
8.	Rotameter, Model F-1500, Gilmont Instruments Inc., Great Neck, NY.
9.	Methanol, methylene chloride, acetone, ethyl acetate, hexane, resi-grade, Baker Chemical Co.
10.	Teflon cartridges, 12 cm X 4 cm Savillex Corpn., Minnetonka, MN.
11.	Tygon tubing, 1 cm i.d. X 1 mm wall X 1.25 cm o.d.
12.	Florisil PR grade 60/100 mesh, Floridin Co.
13.	XAD - 4 resin, Rohm and Haas Co., Philadelphia, PA.

Flux Air Samples

Low volume air samplers (ca 50 lpm) were positioned on a 2.54 cm X 1.5 m mast located in the center of the field to measure flux rates. Air sampler cups were adjusted so that there was a logarithmic progression that consisted of sampling points at 20, 35, 55, 90 and 150 cm above the soil surface. Teflon sampling cups, 4 cm i.d. X 12 cm in length, were fitted with 100 mesh screens in the bottom of each cup. Precleaned XAD-4 (30 ml), a 20-50 mesh macroreticular resin, was placed in each cup. Glass fiber filters were added to the top of the sampling cups during certain periods. Cups were connected to a high volume air sampling pump via tygon tubing (1 cm i.d. X 1 mm wall X 1.25 cm o.d.). The pump was modified with a five port manifold that allowed an air flow rate of approximately 50 liters per minute through each sampler.

Air flow rates were measured at the beginning and end of each sampling period by attaching a rotameter via Tygon tubing and a rubber stopper to the entrance of each sampling cup. The rotameter readings were noted and the flow rates were calculated by using the calibration equation for the rotameter: 0.86 X average reading - 1.2. Total air volumes were calculated from the flow rate multiplied by the length of the sampling period.

High Volume Air Samples

One upwind and two downwind high volume air samplers were run periodically during the time flux samples were taken. Each sample consisted of 100 ml of XAD-4 resin and a 20.3 X 25.4 cm glass fiber filter. Flow rates were approximately 1 m^3/min.

Soil Screen Samples

Soil screen samples consisted of coating a 4 X 10 cm fine mesh screen with a soil slurry made from Yolo sandy loam taken from the same field location prior to this study. The screens were air dried then placed on a piece of plywood to prevent moisture adsorption from the field. Two replicate samples, each consisting of five screens per sample, were placed along side potted parsley plants placed at the four compass points (N,E,S, and W) at positions located 3 meters outside the perimeter of the circle and another set placed 23 meters from the perimeter of the circle at the same compass points.

Potted Parsley Plants

Potted parsley plants from a local nursery, approximately 20 cm in plant height, were placed alongside the soil screens.

Application of Dacthal

Dacthal, 75 W, 11.2 kg/ha was applied on April 9th between 8:30 and 9:45 using a precalibrated ground spray rig. The field was applied in a north-south direction with a 3m boom. Check valves were used to ensure precise shut off at the perimeter of the circle. There was a slight wind out of the north at the beginning of application which became more intense near the completion of the application. High volume air samples were taken on the down and upwind sides of the field during application and for several periods following completion. Flux sampling did not begin until the early evening after the irrigation pipe was laid out.

Irrigation

Irrigation was accomplished by an overhead "rain bird" type commercial system. 9.1 m sections of 10.2 cm diameter pipe were set out in 6.1 m wide rows after the dacthal application was completed. Irrigation did not begin until 24 hours after the application of dacthal. The entire field was irrigated simultaneously. The application rate of water was 0.66 cm/hr, (Table 3).

To prevent transport of dacthal by personnel from the inside of the circular plot, 2.54 cm X 15.2 cm wooden planks were laid out from the center of the circle to the north perimeter of the rectangle so that samplers could be serviced without disturbing the soil.

Laboratory

Extraction of High Volume Air Samples

Resin samples were transferred into 50 ml Erlenmeyer flasks. 150 ml of ethyl acetate (1.5 bed volumes) was added to the flask and the flask was swirled for 30 min. The ethyl acetate was decanted and filtered through Whatman #1 filter paper into a 500 ml round bottom flask. Fresh solvent (100 ml) was added two more times and the flask was again swirled for 15 & 10 minutes. The decanting and filtration process was repeated for each solvent addition. The samples were concentrated using a rotary evaporator. Samples were transferred to an appropriate volumetric flask and the parent compound was analyzed by gas chromatography. A few of the samples were checked for the presence of the transformation products. However, none were detected.

Glass fiber filters were extracted in the following manner. Samples were cut into small squares, with scissors, and transferred to 125 ml Erlenmeyer flasks. Methanol (100 ml) and one drop of concentrated hydrochloric acid was added to each sample. Samples were then blended with a Tissuemizer for one minute. The methanol was decanted and filtered through glass wool and into a 250 ml round bottom flask. Fresh solvent (50 ml) was added to the Erlenmeyer flask and the sample was reblended for one minute. The solvent was combined and evaporated to dryness. Methylene chloride (5 ml) was added and the sample was again evaporated to dryness. Samples were quantitatively transferred to 15 ml centrifuge tubes and taken to dryness. Diazoethane (3 ml) and 10 μl of catalyst (1:3 hydrochloric acid - ethanol) were added. Samples were allowed to stand for 15 minutes then concentrated with a nitrogen evaporator to 0.5 ml. Ethyl acetate was added and the sample was brought to the appropriate volume for analysis using selective ion monitoring (SIM) with a mass selective detector (MSD).

Extraction of Flux Air Samples

Extraction of resin from the flux samples was essentially the same as the high volume air samples with the exception that the volume of ethyl acetate used was 50 ml for all three extractions and the size of the Erlenmeyer flask was 250 ml.

Extraction of the flux filters was the same as for the high volume filters with the following exceptions: The cut up filter was placed in an ignition tube. The samples were extracted with 30 ml of methanol twice.

Extraction of Soil Samples

Soil from screens was first broken up by hand then placed in 500 ml Erlenmeyer flasks. Extraction solution (10 per cent 10 N sulfuric acid in acetone (200 ml) was added and the sample was mechanically swirled for two hours. An aliquot, usually 100 ml, of the extracted soil was transferred to a 250 ml separatory funnel.

A 50 ml portion of water was added along with 5 grams of sodium chloride. The water was extracted three times with 50 ml of hexane. The hexane-acetone extracts were combined, filtered then evaporated to dryness. Methanol (2 ml) was added to the extract and then 4 ml of diazoethane solution. Enough hexane was also added to decrease the polarity of the solvent to the point where the extract just became turbid. The extract was then added to a Florisil micro column and eluted with 5 ml of hexane. The extract was then placed on a second larger Florisil Column and eluted with 60 ml of 6% ether in hexane.

Samples of soil (split samples) were received from CDFA and 50 grams of sample was extracted using the method for the soil screens. However, the pH was raised to 10 and the transformation products were separated. The pH was then lowered to below 1 to extract the parent from the aqueous phase. Samples were then worked up as with the soil screen samples.

Table 3. Irrigation Schedule for Dacthal Project.

DATE	HOURS	cm of WATER
4/10/87	2.6	1.5
4/12/87	2.0	1.3
4/13/87	1.3	0.9
4/14/87	0.9	0.6
4/15/87	2.5	1.7
4/16/87	1.5	1.0
4/17/87	1.1	0.7
4/18/87	1.2	0.8
4/20/87	0.7	0.5
4/21/87	1.1	0.7
4/22/87	1.3	0.9
4/23/87	1.0	0.7
4/24/87	1.1	0.7
4/25/87	1.8	1.2
4/27/87	1.2	0.8
4/28/87	1.7	1.1
4/29/87	1.0	0.7
5/1/87	1.0	0.7
5/2/87	1.0	0.7
5/4/87	1.2	0.8
5/5/87	1.5	1.0
5/6/87	1.5	1.0
5/7/87	1.5	1.0
5/13/87	1.3	0.9
5/15/87	1.5	1.0
5/17/87	1.7	1.1
5/19/87	1.9	1.2
5/22/87	3.0	2.0
5/23/87	2.8	1.9
6/4/87	4.7	3.1
6/9/87-6/12/87	10.6	7.0

Gas Chromatography

The following instruments and detectors were used:

Electron Capture Detector

Hewlett-Packard 5730A equipped with a 30 m x 0.53 mm DB-1 column. Carrier gas, helium, had a flow rate of 12 ml/min and a make up of 27 ml/min. The temperatures were 250, 220, and 300 °C, respectively for the injector, column and detector. The detector was nickel-63.

O.I. (Hall Type) Detector

Hewlett-Packard 5890 equipped with a 30 m x 0.53 mm DB-1 column. Carrier gas, helium, had a flow rate of 6 ml/min with a make up of 15 ml/min. Pyrolysis gas, hydrogen, flow rate was 100 ml/min. Temperatures were 245, 250, and 850 °C, respectively, for the injector, detector base, and pyrolysis oven. The column temperature was held at 180°C for 0.8 min then temperature programmed to 230°C at 10 °C/min and held for 5 min.

Mass Selective Detector

Hewlett-Packard 5890 with a 5970 MSD operated in selective ion monitoring mode (SIM). The column was a 12 m capillary methyl silicone with a flow rate of 0.68 ml/min operated in splitless mode. Injector and transfer line temperatures were 275 and 250 °C, respectively. Column temperature was held at 50 °C for 2.5 min then programmed at 30°C/min to 250°C for 5 min. Two groups of ions were monitored using SIM. Group I (Parent and mono acid derivative) consisted of the following ions: 299, 301, 303, 313, and 315. Group II (diacid derivative) ions consisted of 313, 315, 317, 358, and 360. Group I was monitored from 2.5 min to 9.7 min while Group II monitoring began at 9.7 min.

High volume and flux resin samples were analyzed using the electron capture detector. High volume filter samples were analyzed by MSD while the flux filter samples were analyzed using the O.I. detector. The O.I. detector was also used to analyze soil samples (screens) and to check for transformation products in the soil matrix. Recoveries for each matrix and the trapping efficiencies for low and high volume air samplers are given in Table 4.

Table 4. Recovery of Dacthal and Transformation Products.

Matrix	Chemical	Amount Spiked	Recovery (%) 1	2	3	4	avg	std
HV Filter	dacthal	5.0 μg	82	71	65	75	73	6.9
	mono acid	5.0	78	66	64	79	72	7.6
	di acid	5.0	73	62	67	76	70	6.2
Flux Filter	dacthal	1.0	93	93	95	--	94	1.2
	dacthal	2.5	92	92	90	--	91	1.2
	mono acid	1.0	92	92	93	--	92	0.58
	mono acid	2.5	90	87	88	--	88	1.5
	di acid	1.0	68	60	57	--	62	5.7
	di acid	2.5	68	63	66	--	66	2.5
XAD-4	dacthal	0.8	112	--	--	--	--	--
Resin	dacthal	4.0	105	98	98	--	100	4.0
Soil Screen	dacthal	5.0	100	103	99	--	101	2.1
		1.0	91	74	87	--	84	8.9
	mono acid	5.0	99	74	69	--	81	16
		1.0	94	71	79	--	81	12
	di acid	5.0	109	60	26	--	65	42
		1.0	31	47	26	--	35	11
<u>Trapping Efficiency</u>								
Low Volume XAD Resin Dacthal		82	93	92	120	91	95	11
High Volume Air (filter/resin)		85	82	91			86	3.7

Results

High Volume Air Samples

Downwind concentrations in air ranged from 910 ng/m^3 of dacthal (day 1) to 22 ng/m^3 (day 3) for the resin. Filters contained 420 ng/m^3 on day 0 and were at a minimum of 5.8 ng/m^3 on day 11 (Figure 3, Table 5). Most of the dacthal was found in the resin. There were some small amounts of dacthal on some up-wind high volume samples when the winds were light and switching erratically from north to south during a four or five hour sampling period, but generally the upwind sample had insignificant amounts of dacthal.

While there was dacthal detected in the air samples taken during onion harvest, the concentrations in all these samples were less than 0.5 ng/m^3, the limit of detection for the method. There were no detectable quantities of the transformation product in any of the air samples.

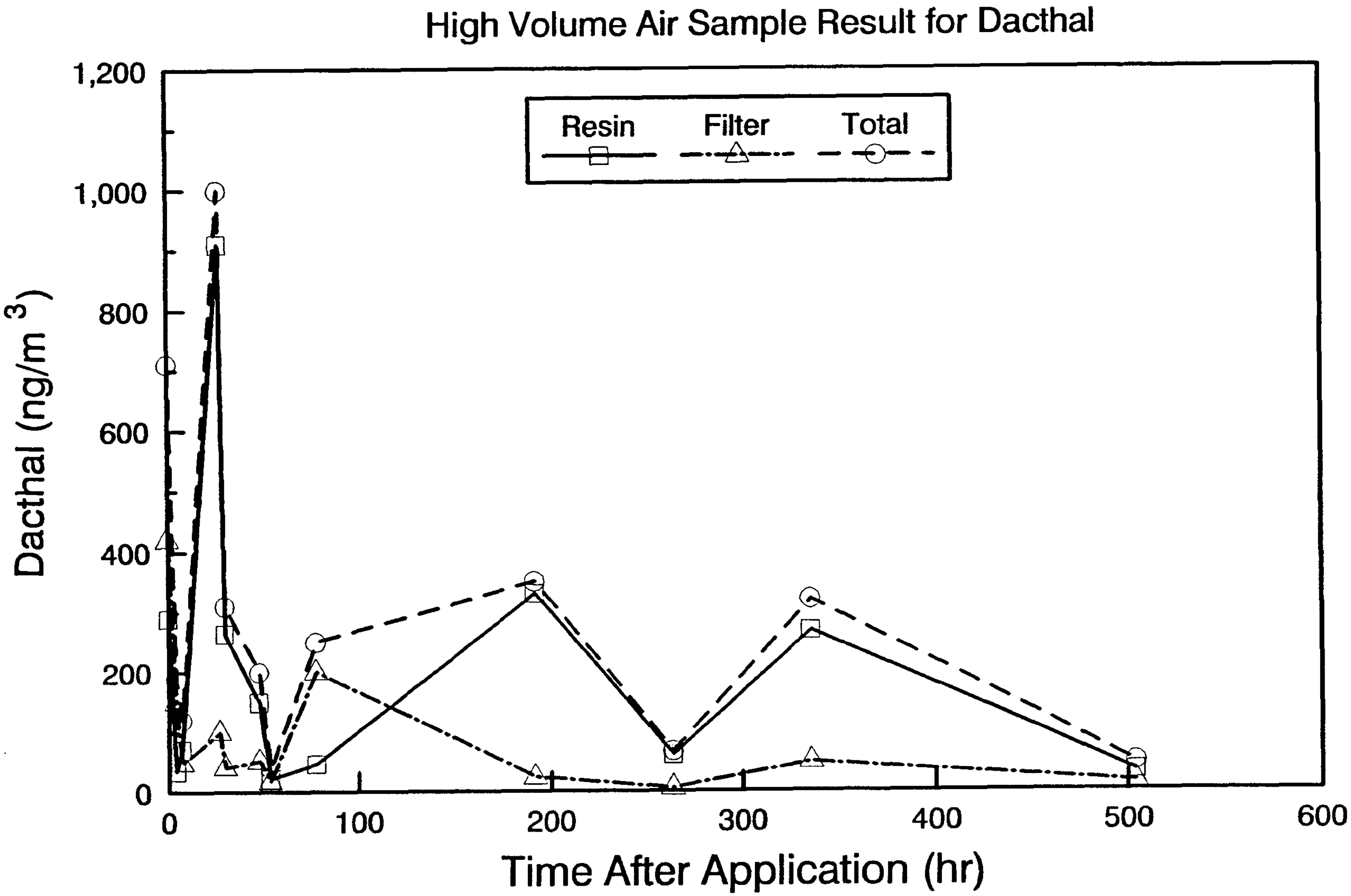

Figure 3. Downwind High Volume Air Samples

Table 5. Downwind High Volume Air Samples (ng/m^3), Average of Two Replicates.

DAY	TIME AFTER APPLICATION	RESIN	FILTER	TOTAL	IRRIGATION (+ OR -)
0	0	290	420	710	-
0	4	35	150	190	-
0	7	71	48	120	-
1	27	910^A	100	1000	+
1	30	260	41	310	+
2	48	150	52	200	-
2	54	22	18	39	-
3	78	47	200	250	-
8	192	330	24	350	+
11	264	61	5.8	67	+
14	336	268	49	320	+
21	504	33	15	48	-

A: One Replicate

Flux Resin Samples

Table 6 contains dacthal low volume air concentrations in $\mu g/m^3$, for the flux samplers while Table 7 contains the wind speed, direction, temperature and differential air temperature.

Table 8 contains the data, and result of flux calculations by both the Thornthwaite-Holzman (TH) and Theoretical Profile Shape (TPS) methods of calculation. The basis, equations, and calculation methods are published (Majewski et. al.). Results for the two methods are generally in fair agreement with the TPS results, averaging about 20% higher than those from the TH calculation. This differential was also observed in a prior field comparison of the two calculation methods reported in Appendix 1.

Plots of dacthal flux and dacthal cumulative flux are in Figures 4 and 5, using data from both the aerodynamic (TH) and circular plot (TPS) methods of calculation. The cumulative flux reports results in grams lost from the field plot per sampling period (rather than per hour) and, thus, the data for later periods appears larger than that from earlier periods because of the longer sampling periods used in the later measurements. Also, each of the later sampling periods followed a scheduled irrigation so that the soil was always moist (thus optimizing the chance for volatilization to occur) whereas some of the earlier sampling periods (April 11 and 12) were conducted when the soil surface was fairly dry (cf. Table 3).

The aerodynamic flux was calculated using the following equations:

$$Ri = \frac{g\,(\delta T/\delta z)}{T\,(\delta u/\delta z)^2}$$

for unstable conditions $(\delta T/\delta z) < 0$:

$$\phi_m = (1 - 16Ri)^{-0.333}$$

$$\phi_c = 0.885(1 - 22\,Ri)^{-0.40}$$

for stable conditions: $(\delta T/\delta z) > 0$

$$\phi_m = (1 = 16Ri)^{+0.333}$$

$$\phi_c = 0.885(1 + 34Ri)^{0.40}$$

for neutral conditions $\delta T/\delta z = 0$, $Ri = 0$

$$P = \frac{k^2(\bar{c}_1 - \bar{c}_2)(\bar{u}_2 - \bar{u}_1)}{\phi_c\phi_m[\ln(z_2/z_1)]^2}$$

P is the vertical pesticide flux ($\mu g\ m^{-2}\ hr^{-1}$)

k is von Karman's constant (dimensionless, ~ 0.4)

$\bar{c}$ is the pesticide air concentration ($\mu g/m^2$) at height z(m)

u is the horizontal wind speed (ms^{-1}) at z

ϕ_c is the diabatic pesticide correction function

ϕ_m is the diabatic momentum correction function

Ri is Richardson number, a stability parameter

g is the gravitational acceleration (ms^{-2})

T is the ambient air temperature at the flux plane in K

z_1 is the lower height of flux plane, z_2 is the upper height of the flux plane

Table 6. Flux Resin Air Concentration Results ($\mu g/m^3$).

DAY OF APRIL	TIME	Height (cm) 20	35	55	90	150
9	1845-2045	1.25	0.66	0.53	0.048	0
9	2130-2330	0.229	0.154	0.12	0.006	0.005
10	0000-0650	0.212	0.13	0.105	0.067	0.025
10	1400-1600	2.55	2.45	2.25	0.912	0.832
10	1630-1830	1.28	0.739	0.781	0.57	0.454
10	1900-2100	0.636	0.55	0.432	0.377	0.213
11	0700-0930	0.58	0.36	0.25	0.21	0.15
11	1000-1300	0.675	0.457	0.288	0.096	0.093
11	1330-1630	0.0193	0.0153	0.0068	0.0047	0.0043
11	1700-2000	0.0682	0.040	0.042	0.0233	0.016
11	2030-2330	0.0564	0.0453	0.0422	0.0187	0.0123
11	2345-0645	0.32	0.024	0.019	0.013	0.008
12	0715-1300	0.026	0.023	0.017	0.014	0.008
12	1330-1530	0.049	0.032	0.03	0.024	0.013
13	1345-2000[A]	3.4	2.4	1.8	1.3	0.8
14	1100-1700	3.81	2.95	2.62	1.80	1.15
17	1215-1400	2.05	1.65	1.20	0.71	0.40
20	1200-1830	1.7	1.62	1.23	0.99	0.53
23	1115-1815	1.48	1.19	0.91	0.56	0.36
30	0930-1630	0.468	0.358	0.221	0.214	0.085

A: Air samplers run but no flux calculations made due to loss of wind speed data.

Table 7. Meteorological Data for Each Flux Period.

DAY OF APRIL	START TIME	WIND SPEED (cm/sec)[A] U20	U55	U90	U150	UDir[B]	Temp	dT[C]
9	1845	65.6	71.7	85.7	109.8	113	22.0	0.419
9	2130	43.3	46.9	53.3	73.8	107	14.0	0.187
10	0	53.4	66.1	76.3	90.4	66	10.2	0.296
10	1415	316.4	385.3	426.6	466.9	155	27.2	0.012
10	1630	413.4	507.9	552.7	563.9	121	21.2	0.115
10	1900	220.8	275.5	301.6	327.8	175	17.5	0.208
11	700	473.4	473.9	428.9	501.1	268	11.3	0.049
11	1000	652.3	715.8	724.3	726.4	275	17.3	-0.472
11	1330	435.5	546.0	576.7	626.7	268	22.5	-0.816
11	1700	295.7	366.1	380.8	422.7	273	20.0	-0.058
11	2030	118.0	151.8	173.4	199.5	248	11.1	0.414
12	2345	587.7	758.2	814.3	884.5	264	12.6	0.338
12	715	601.1	763.8	812.3	874.7	271	19.0	-0.548
12	1330	447.4	561.8	595.8	636.3	265	26.8	-1.165
14	1100	135.7	158.2	167.1	174.2	188	26.9	-0.298
17	1215	458.0	563.3	594.1	633.8	114	24.4	-0.312
20	1200	129.6	151.5	162.4	168.0	212	29.1	-0.409
23	1115	314.3	383.2	402.0	426.7	90	24.7	-0.322
30	930	465.6	580.2	612.7	655.2	116	20.1	-0.623

A: U20, U55, U90, and U150 are the wind speed at 20, 55, 90 and 150 cm, respectively.
B: Wind Direction: 0° = East: 90° = South: 180° = West: 270° = North
C: Differential Air Temperature.

Table 8. Data for Flux Calculations Using Thornthwaite Holtzman (TH) and Theoretical Profile Shape (TPS) Methods.

Run Time (hr)	Day of April	Start Time	Wind Speed cm/s U_{30}	U_{80}	U_{150}	Ri	Dacthal $\mu g/m^3$ C_{30}	C_{80}	C_{150}	Flux $\mu g/m^2.hr$ TH	TPS
2.00	9	1845	64.8	89.6	109.8	0.114	0.490	0.140	0.001	23.2	0.3
2.00	9	2130	40.9	59.0	73.8	0.098	0.181	0.077	0.005	5.4	1.1
6.80	10	0	58.0	76.3	90.4	0.153	0.145	0.073	0.025	3.0	6.6
2.00	10	1415	344.4	417.8	466.9	0.000	2.510	1.530	0.832	508.2	1126.0
2.00	10	1630	450.4	530.1	563.9	0.003	1.080	0.662	0.454	224.3	742.1
2.00	10	1900	242.7	294.9	327.8	0.013	0.565	0.385	0.213	54.3	202.4
2.40	11	700	218.9	556.7	501.1	0.000	0.368	0.226	0.150	340.4	217.9
3.00	11	1000	672.6	715.9	726.4	-0.043	0.519	0.142	0.093	179.5	195.8
3.00	11	1330	477.4	570.2	626.7	-0.016	0.016	0.005	0.004	8.7	7.8
3.00	11	1700	321.3	382.0	422.7	-0.003	0.057	0.030	0.016	11.9	19.6
3.00	11	2030	131.3	170.9	199.5	0.045	0.048	0.025	0.012	3.7	7.1
7.00	11-12	2345	653.6	798.7	884.5	0.003	0.026	0.015	0.008	10.8	20.5
5.75	12	715	663.4	797.8	874.7	-0.005	0.023	0.014	0.008	9.2	20.3
2.00	12	1330	491.1	584.5	636.3	-0.022	0.042	0.025	0.013	14.8	24.0
6.0	14	1100	144.6	163.8	174.2	-0.133	3.271	1.982	1.156	443.2	583.8
3.75	17	1215	498.2	584.7	633.8	-0.007	1.728	0.892	0.357	562.5	655.9
6.5	20	1200	138.4	157.9	168.0	-0.174	1.730	1.010	0.530	292.3	258.1
7.25	23	1115	340.4	395.9	426.7	-0.017	1.260	0.681	0.300	281.5	371.1
7.0	30	930	509.2	602.6	655.2	-0.012	0.394	0.230	0.085	126.6	161.4

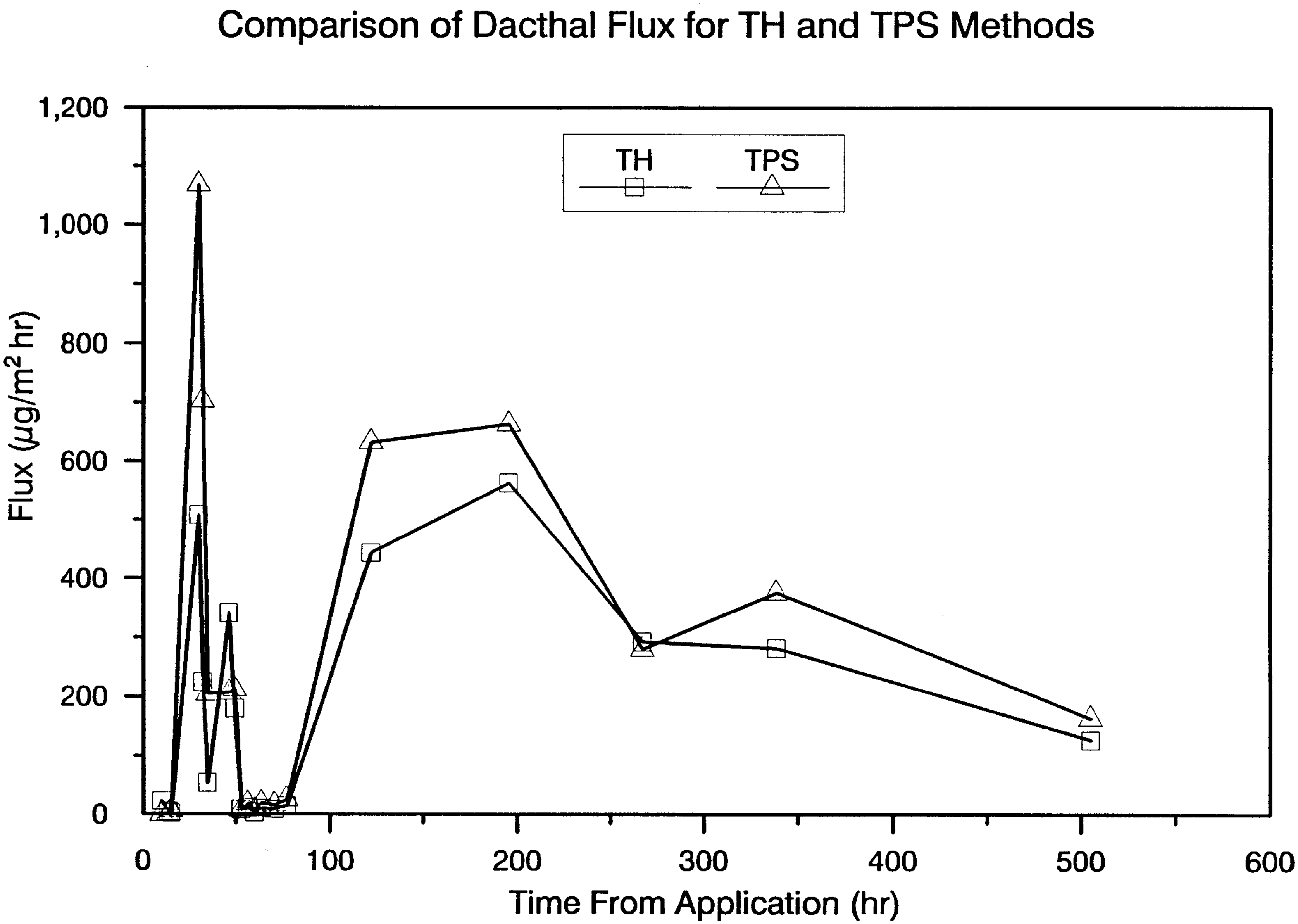

Figure 4. Flux of Dacthal

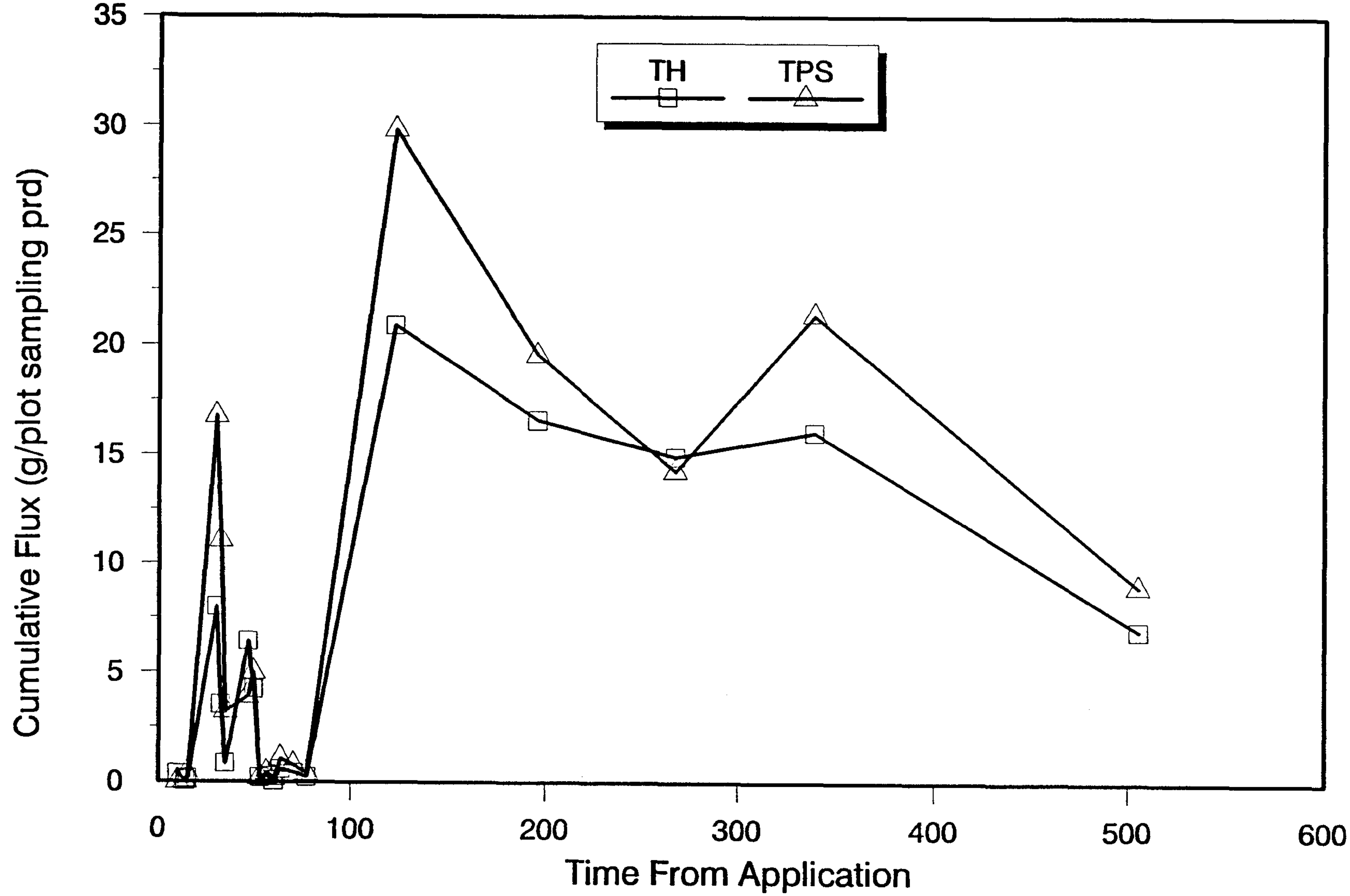

Figure 5. Cumulative Flux of Dacthal

Table 9 presents a summary of the measured volatilization flux for dacthal from the field plot in three units ($\mu g/m^2/hr$, g/hr/plot, and g/plot) using the TH and TPS flux calculation methods. Table 9 also presents the total g/plot lost by volatilization for the measured sampling periods for each day when measurements were taken.

Table 10 repeats some of the Table 9 values, but then places the results for the days on which measurements were made on a 12 hour basis (i.e. grams volatilized from the plot, 12 hr/day basis). The assumption here is that significant volatilization occurred only during daylight hours. No account was made for the time of each day that sprinkle irrigation was made (during which, presumably, little volatilization occurred) although that adjustment could be made from Table 3 data. Table 10 then adds extrapolated flux values (12 hour basis) for those days when no measurements were made, with the extrapolation done by averaging measured fluxes on the days bracketing those when no measurements were made. Table 10 then sums the total grams of dacthal lost from the field plot by volatilization over the 21-day measurement period.

Table 11 presents the results from CDFA analysis of field soil, from which the decline of dacthal from soil by all processes can be estimated by regression. Extrapolating the regression time to time 0 yields an initial dacthal soil residue of 5.08 kg. The stated application rate was 9 kg, so that about 4 kg was lost either by drift during application or by rapid volatilization from soil before soil sampling (and flux measurements) could be made. This lag was due to the time it took to apply dacthal, and also to water it on the application day.

Assuming a 5.64 kg initial soil load, and that 2.09 kg of this was lost during the 21 day period by all processes (Table 11), one can calculate the fraction of the total loss due to volatilization. That calculation is as follows:

$$\text{TH method:} \quad \frac{550.7 \text{ volatilized}}{2020 \text{ g lost by all processes}} = 27.3\%$$

$$\text{TPS method:} \quad \frac{673.5 \text{ g volatilized}}{2020 \text{ g lost by all processes}} = 33.3\%$$

Table 9. Summary of Measured Volatilization Flux by TH and TPS Methods.

Day of April		Time Period	Run Time (Hr)	Measured Flux μg/m²/hr TH	TPS	g/hr/plot[A] TH	TPS	g/plot[B] TH	TPS
9	(0)	1845-2045	2.0	23.2	0.3	0.18	0.002	0.36	0.005
9	(0)	2130-2330	2.0	5.4	1.1	0.042	0.009	0.085	0.017
						Total		0.445	0.032
10	(1)	0000-0650	6.8	3.0	6.6	0.024	0.052	0.16	0.35
10	(1)	1415-1600	2.0	508.2	1126.0	3.99	8.84	7.98	17.69
10	(1)	1630-1830	2.0	224.3	742.1	1.76	5.83	3.52	11.66
10	(1)	1900-2100	2.0	54.3	202.4	0.43	1.59	0.85	3.18
						Total		12.51	32.88
11	(2)	700-0930	2.4	340.4	217.9	2.67	1.71	6.42	4.28
11	(2)	1000-1300	3.0	179.5	195.8	1.41	1.54	4.23	4.61
11	(2)	1330-1630	3.0	8.7	7.8	0.068	0.06	0.21	0.18
11	(2)	1700-2000	3.0	11.9	19.6	0.093	0.15	0.28	0.46
11	(2)	2030-2330	3.0	3.7	7.1	0.029	0.056	0.087	0.17
						Total		11.49	9.70
12	(3)	2345-0645	7.0	10.8	21.5	0.085	0.17	0.59	1.18
12	(3)	0715-1300	5.75	9.2	20.3	0.072	0.16	0.42	0.92
12	(3)	1330-1530	2.0	14.8	24.0	0.12	0.19	0.23	0.38
						Total		1.24	2.48
14	(5)	1100-1700	6.0	443.2	583.8	3.48	4.59	20.89	27.51
17	(8)	1215-1400	3.75	562.5	655.9	4.42	5.15	16.57	19.32
20	(11)	1200-1830	6.5	292.3	258.1	2.29	2.03	14.92	13.18
23	(14)	1115-1815	7.25	281.5	371.1	2.21	2.91	16.03	21.13
30	(21)	930-1645	7.0	126.6	160.7	0.99	1.26	6.96	8.83

A: Plot area = 7854 m^2
(g/hr/plot = ($\mu g/m^2$/hr-1)(7854 m^2plot)(10^{-6}g/μg)

B: (g/plot/period) = (g/hour/plot)(run time)

Table 10. Summary of Measured and Extrapolated Flux on 12 Hr/Day Basis by TH and TPS Methods.

Day of April		Measured[A] g/plot TH	TPS	Measurement Run Time (hr)	Extrapolated[B] g/plot -- 12 hr basis TH	TPS
9	(0)	0.445	0.032	4	1.33	0.096
10	(1)	12.51	32.88	12.8	11.73	30.83
11	(2)	11.49	9.70	14.4	9.58	8.08
12	(3)	1.24	2.48	14.75	1.01	2.02
13	(4)	--	--	0	21.40	28.52
14	(5)	20.89	27.51	6.0	41.78	55.02
15	(6)	--	--	0	47.40	58.42
16	(7)	--	--	0	47.40	58.42
17	(8)	16.57	19.32	3.75	53.02	61.82
18	(9)	--	--	0	40.28	43.08
19	(10	--	--	0	40.28	43.08
20	(11)	14.92	13.18	6.5	27.54	24.33
21	(12)	--	--	0	27.04	29.65
22	(13)	--	--	0	27.04	29.65
23	(14)	16.03	21.13	7.25	26.53	34.97
24	(15)	--	--	0	19.23	25.06
25	(16)	--	--	0	19.23	25.06
26	(17)	--	--	0	19.23	25.06
27	(18)	--	--	0	19.23	25.06
28	(19)	--	--	0	19.23	25.06
29	(20)	--	--	0	19.23	25.06
30	(21)	6.96	8.83	7.0	11.93	15.14
				Total	550.7	673.5

A: From Table 9 (g/plot/period) totals, = Σ(g/plot/period)

B: Normalized measurement periods of < 1 hrs to 12 hrs; measurement periods of > 12 hr were not normalized to 12 hr; periods where no data was collected was estimated as averages of preceding and following sampling days.

Table 11. Decline of Dacthal in Field Soil Based on CDFA Soil Analyses.

Day After	Measured Values kg/Field[a]			Regression Values kg/Field[b]		
Application	Actual	Log	Delta Loss	Actual	Log	Delta Loss
0	4.65	0.671	0.06	5.08	0.706	0.00
1	4.77	0.679	-0.06	4.97	0.696	0.11
7	3.71	0.569	1.00	4.29	0.632	0.79
14	3.77	0.576	0.94	3.61	0.558	1.47
21	2.77	0.443	1.94	3.06	0.485	2.02
42	2.14	0.331	2.57	1.83	0.263	3.25
63	1.27	0.104	3.44	1.10	0.041	3.98
84	0.81	-0.090	3.90	0.66	-0.181	4.42
168	0.071	-1.148	4.64	0.09	-1.068	4.99

[a] Assume initial concentration (from average of days 0 and 1) = 4.71 kg/field.

[b] Assume initial concentration = 5.08 kg/field. Amount lost after 21 days, based on the regression equation, is 2.02 kg/field.

Flux Filter Samples

Flux filter sample results are reported in Table 12. Filter results were approximately 5 per cent of the total airborne dacthal found during those periods run immediately after irrigation. Filter results were as high as 70 per cent of the total airborne dacthal found during periods of dry conditions.

However, the values generated did not give good linear results when plotted against the log of the height and, therefore, flux was not calculated. One explanation may be that these flux calculations were developed for molecules that are in a vapor phase.

Table 12. Flux Filter Results ($\mu g/m^3$).

		Height (cm)				
DAY:	TIME	20	35	55	90	150
9	1845-2045	B	B	B	B	B
9	2130-2330	0.0575	0.0483	0.0247	0.0116	A
10	0000-0650	0.0265	0.0204	0.022	0.0011	A
10	1400-1600	0.126	0.101	0.0913	0.0575	A
10	1630-1830	0.171	0.090	A	0.0482	0.0134
10	1900-2100	0.153	0.162	0.0995	0.054	A
11	0705-0930	B	B	B	B	B
11	1000-1300	B	B	B	B	B
11	1330-1630	0.0226	0.0228	0.042	0.034	A
11	1700-2000	0.0396	0.0243	0.214	0.0015	A
11	2030-2330	0.0491	0.0509	A	0.0219	0.0022

A: Sample below limit of detection, or lost
B: No filter samples taken during sampling period

Soil Screens

The first batch of soil screens were set in place after the completion of the dacthal application and collected 24 hours later. A second batch was set in place as the first set was collected. However, a rain shower during the evening of April 10 washed all the soil off of the screens. Another batch was set in place on April 14 and collected on April 19.

Background screens had an average of 3.7 ng/cm^2 dacthal. The highest concentration was found on screens to the north, 3 m from the perimeter of the circular plot (Table 13), collected 10 days after application (118 ng/cm^2). Screens to the south had roughly equal concentrations at both 3m and 23 m, of approximately 57 ng/cm^2. There was no transformation products detected above the detection limit.

Parsley Plants

Parsley plants that were placed next to the soil screens were analyzed by the CDFA chemistry lab. The results will be reported separately by CDFA.

Table 13. Soil Screen Results (ng/cm²).

	Location (from circle center)	East 1	East 2	East Avg	South 1	South 2	South Avg	West 1	West 2	West Avg	North 1	North 2	North Avg
4/9/87	3 m	6.9	10.2	8.55	38.5	47.0	42.8	2.7	0.5	1.6	7.4	3.2	5.3
	23 m	5.1	7.4	6.25	11.9	6.7	9.3	2.5	--	2.5	4.1	2.0	3.05
4/19/87	3 m	24.8	17.7	21.3	57.7	55.7	56.2	8.8	9.8	9.3	121	116	118
	23 m	52.6	--	52.6	64.0	54.8	59.4	3.6	3.4	3.5	66.1	6.7	35.4

DISCUSSION

Dacthal was measurably lost from the treated circular onion plot by volatilization for at least the first 21 days following application. How much was actually lost during the 21 days can only be crudely estimated because flux measurements were only conducted for several hours on some of the days in that 21 day interval. Using the data from the actual periods during which flux samples were taken, leads to a calculated loss of either 101.1 g/plot (TH method) or 135.1 g/plot (TPS method). We favor the higher figure based on the results of prior studies although, given the error associated with flux determination, the two numbers are probably not significantly different.

Uncertainty also exists in the amount of dacthal actually deposited on the soil surface. The stated application rate (10 lbs/acre) leads to an initial deposit of 9 kg on the 0.785 ha plot. Actual analysis of soil samples by CDFA, however, indicates that the initial deposit was approximately 5 kg. In reality, some dacthal may have been lost by drift during application or deposited but then rapidly lost by volatilization in the time which lapsed between application and soil sampling -- a period during which no flux measurements could be made because application equipment was still in the field. Neglecting this perhaps substantial early loss, by both drift and rapid volatilization, and assuming that ca 5 kg was in fact the initial deposit, one can calculate that 2.02 kg was lost from the soil by all processes by regressing data from CDFA's soil analysis during the initial 21 day period. Of this 2.02 kg, 5-7% was accounted for as volatilization flux during the hours when flux measurements were taken. However, those hours were only a small fraction of the total daylight hours during which flux was possible. Accounting for this, the actual flux loss was much higher -- perhaps 27 to 33% of the total lost by all dissipation processes. This is in keeping with an earlier report in which 2% was lost by volatilization in 34 hr from moist soil (Glotfelty et al 1984), and is in contrast with the generalization that volatilization is an insignificant loss pathway for dacthal (Herbicide Handbook of the Weed Society of America, 1983). An additional loss to the atmosphere occurred by wind erosion of surface soil dust, but the magnitude could not be estimated from the data at hand.

Downwind air samples confirm the movement of dacthal vapors and, to a lesser extent, particulate matter out of the treated plot over the same 21 day period. Analysis of soil screens confirmed the downwind deposition of dacthal vapors and/or particulate matter. The highest deposition value was ca 60 ng/cm^2 or 600 $\mu g/m^2$. Only a wild estimate of what this deposition could mean for a downwind mature plant is possible. For a large plant with 1 m^2 of foliar surface area, weighing 1 kg, in the range expected for a mature parsley plant, estimate leads to 0.6 ppm by downwind deposition. This assumes that the capture efficiency for parsley is the same as for soil (which is reasonable) and holds for a parsley plant in close proximity to a dacthal-treated field. Thus, the hypothesis that downwind deposition of dacthal not associated with spray drift contributes a measurable residue load to a non-target crop appears reasonable.

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