Herbicide Residues on Strawberries: The Effects of Combinations of Dacthal and Sesone

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Combinations of herbicides are often necessary for growers to obtain efficient weed control in strawberries. Consequently, researchers at the Ohio Agricultural Research and Development Center (OARDC), as well as at other experiment stations and research facilities, are considering the effects of herbicides in combinations in the attempt to provide an expanded spectrum and duration of weed control. Such studies must consider several factors relative to the possible interaction of chemicals including the compatability of the materials in application and any changes in properties of the solution that might promote adverse synergistic or potentiating effects affecting the toxic characteristics or resulting in excess herbicide residues at harvest. Of concern also are the possibilities of creating similar conditions as a result of the grower applying several pesticides singly, but at the approximate same time over the same crop area.

Researchers at OARDC investigating weed control in strawberries were concerned with the combinations of Dacthal (dimethyl tetrachlorothiolate) and Sesone (2,4-dichlorophenoxyethyl sulfate). Dacthal, a pre-emergent herbicide, is effective for the control of certain broadleaf weeds and annual grasses when used according to label directions. Sesone is a pre-emergent herbicide of the 2,4-D family that is considered milder in reaction than 2,4-D and has longer effective duration due to its conversion to 2,4-D in the soil. Both herbicides had a registered use on strawberries and a tolerance of 2 ppm each on the fruit, reflecting the relative safety and effectiveness of each individually. The study reported herein was initiated to determine any potentiating effects on residues at harvest when Dacthal and Sesone (or any similar 2,4-D product) are used in combination.

EXPERIMENTAL METHODS

Treatment and collection of samples. Established replicate strawberry plots of the cultivar Pocahontas were treated with combinations of Dacthal and Sesone as indicated in Table 1. Samples of ripe strawberries were then collected the following growing season, placed in plastic bags and stored in a freezer until analyzed.

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Analytical procedures.

a. Determination of Dacthal residues. A very simple, rapid, and sensitive gas chromatographic procedure was developed for the analysis of Dacthal residues following the preliminary investigations of existing methods (1), of the simultaneous analysis for Dacthal and Sesone from the same extraction, and of the elution characteristics of Dacthal from florisil, polyethylene-coated alumina, neutral alumina, and silica gel. Fifty gram samples of strawberries were blended at high speed for 3 to 4 minutes with 200 ml of glass distilled benzene. The extract was centrifuged at 2200 RPM for 15 minutes and the supernatant pipetted off and retained in a volumetric flask. Fifty-ml of benzene extract was concentrated by a flash rotating evaporator to a small volume and then placed on a benzene prewashed 4 to 5 inch layer of Davison No. 928, 100-200 mesh silica gel capped with 1 inch of anhydrous sodium sulfate in a 20 x 250 mm reservoired chromatography column. The Dacthal was eluted from the column with 80 ml of benzene, was concentrated to a small volume, and aliquots injected on the gas chromatographic column.

The F & M Model 400 Biomedical Gas Chromatograph was operated with a 4-ft. long, 1/4-in. diameter glass column of 3.8% SE-30 on Diataport S at the column temperature of 192° C and electron capture detector temperature of 210° C. At a range of 10 and attenuation of 8 on the electrometer and a pulse interval of 50 the retention time was approximately 42 seconds from the beginning of the solvent peak and gave a sensitivity of 80% recorder scale deflection for 0.9 ng of Dacthal. The recovery of Dacthal from strawberry samples fortified at concentrations from .02 to 2.0 ppm Dacthal ranged from 80 to 120 percent and averaged 93 percent.

b. Determination of Sesone and 2,4-D residues. Efforts to determine Sesone hydrolysis residues in strawberries by gas chromatographic analysis of derivatives were not successful. Investigations with the methylene blue chloride colorimetric method (1) were frustrating, in that long-lasting, strong emulsions formed when extracting the aqueous strawberry solution with chloroform. The emulsions reoccurred to a certain extent when the color was developed with methylene blue chloride solution causing somewhat persistent turbidity in the solution. In addition the reagent blanks and control samples frequently had absorbance values equal to recovery samples which prevented quantitative determination. It was thus decided to analyze for 2,4-D residues because that chemical is included in the metabolism or degradation pathway of Sesone (2).

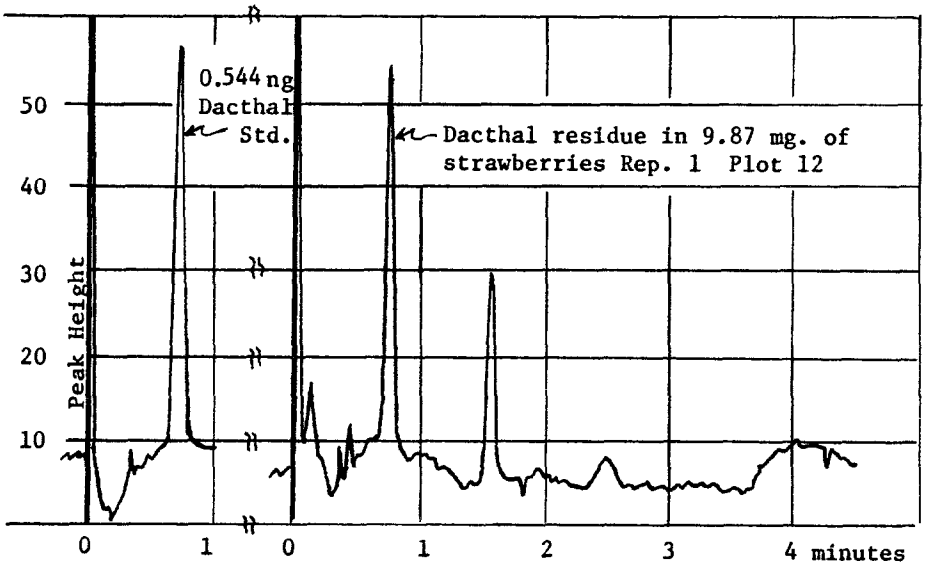

Fig. 1. Characteristic gas chromatograms of Dacthal Standard and of residue in field plot strawberry samples. F & M Model 400 Biomedical GLC with 4 ft., 1/4 in. glass column of 3.8% SE-30 on Diataport S. Column Temp. 188° C; Detector Temp. (Electron Capture) 210° C; Electrometer setting: Range 210, Attenuation 8, Pulse Interval 50; Carrier Gas: Argon - Methane at 60 cc/min.

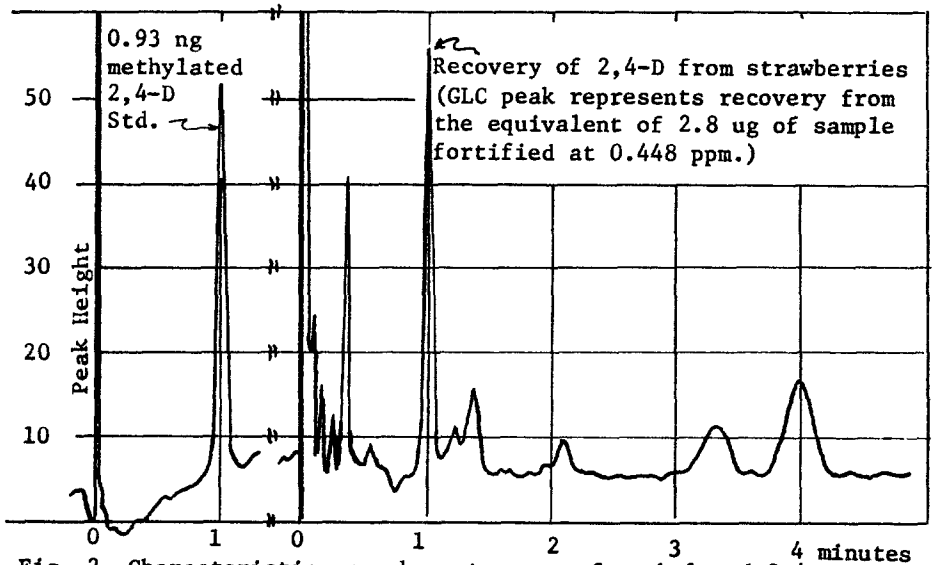

Fig. 2. Characteristic gas chromatograms of methylated 2,4-D Standard and of recovery from strawberry sample. Barber Colman Series 5000 GLC with 4 ft., 1/4 in. glass column of (1:1 mix) 10.47% DC-200 + 15.14% QF-1 on Gas Chrom Q. Column Temp. 170° C; Detector Temp (Electron Capture) 210° C; Electrometer setting: Range 100, Attenuation 2; Carrier gas: nitrogen at 100 cc/min.

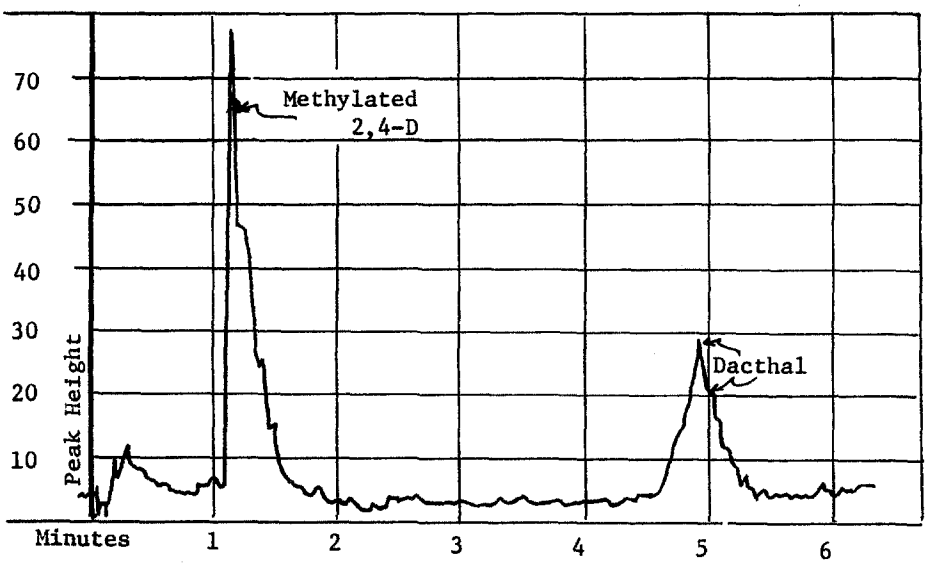

Fig. 3. Gas chromatogram of methylated 2,4-D and Dacthal Standards as determined by the Microcoulometric Detector. Operating conditions: GLC- as in Figure 2 with column temp. 161° C and N_2 flow at 120 cc/min; Microcoulometer: Bias 260 mv, Range 100 ohms, Combustion temp. 800° C. Inlet temp. 300° C, Oxygen and Nitrogen flow at 1.5 on flow rotameters.

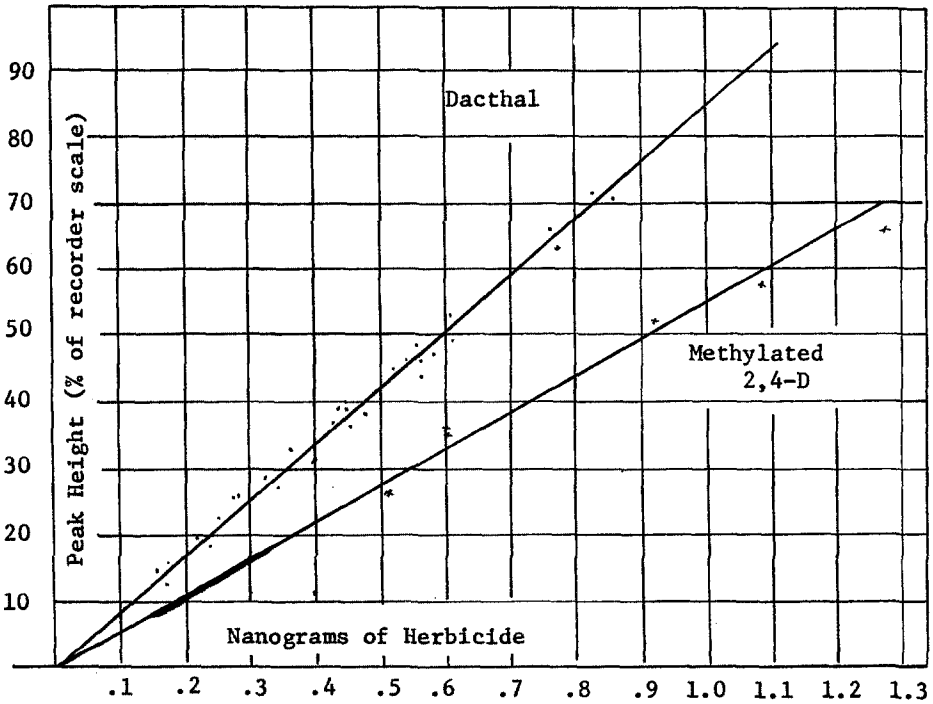

Fig. 4. Typical Standard Curves for Dacthal and Methylated 2,4-D as measured by the Electron Capture Detector.

Fifty-gm samples of ripe, cleaned strawberries were blended with a solution consisting of 150 ml of water, 10 ml of 40% phosphotungstic acid, and 10 ml of concentrated hydrochloric acid for 3 to 4 minutes. The pulp was separated by centrifuging at 2000 RPM for 10 minutes and all the aqueous solution was used in the analysis.

The aqueous solution was extracted 3 times with 50 ml aliquots of purified chloroform and the combined chloroform extract gently evaporated to dryness. The residue was dissolved in 1 ml of methanol and 5 ml of diethyl ether, and transferred to a 15 ml centrifuge tube. A small generator consisting of 2 stoppered test tubes with connecting glass tubing was used to methylate the solution with diazomethane. Two ml of 60% aqueous KOH, 2 ml of distilled carbitol, and 2 ml of diethyl ether were placed in the second test tube. Approximately 30-50 mg of Diazald on the end of a micro spatula was added to the solution in this tube and the apparatus rapidly connected. Nitrogen, first bubbled through a few ml of diethyl ether in the first tube, bubbled into the solution in the generator and then carried the generated diazomethane on through the system where it bubbled into the sample in the centrifuge tube for 3 minutes.

The excess diazomethane was removed by evaporating the sample to dryness with a gentle air stream. The residue was taken up in 5 ml of hexane and passed through a 10 x 250 mm column containing 2 inches of activated florosil (Kensco Scientific Corp., activated at 650° C). The material on the column was washed with an additional 10 to 15 ml of hexane and the methylated 2,4-D then eluted with 25 ml of diethyl ether. Aliquots of the eluate were injected on a 4 ft. long, 1/4 in. diameter glass column of 1:1 mixture of 10.47% DC-200 plus 15.14% QF-1 on 100-200 mesh Gas Chrom Q. The oven of the Series 5000 Barber Colman gas chromatograph was operated at 170° C with the tritium foil electron capture detector at 210° C. Methylated 2,4-D had a retention time of 1 minute from the beginning of the solvent peak under these conditions. Recovery values of 2,4-D at concentrations of 0.1 to 2.2 ppm ranged from 70 to 116.0 percent and averaged 84 percent.

RESULTS AND DISCUSSION

Characteristic chromatograms of Dacthal and 2,4-D residues on strawberries and standard solutions are shown in Figures 1 and 2. Confirmation of presence of the two residues was accomplished by microcoulometric detection after separation on the gas chromatographic system used for 2,4-D (Figure 3).

TABLE 1

Dacthal and 2,4-D Residues in Ripe Strawberries OARDC, Wooster, Ohio

Sample No.		Treatment			Date Sampled	Residues (PPB)	
			lbs/A				
Rep.	Plot	Date - 1965	Dacthal	Sesone	1966	Dacthal	2,4-D
I	4	-	0.0	0.0	June 27	4.5[a]	22.6[a]
II	34	-	0.0	0.0	"	6.6[a]	25.4[a]
III	47	-	0.0	0.0	"	0.0	26.0[a]
IV	70	-	0.0	0.0	"	9.7[a]	-
I	1	Sept.	8.0	0.0	July 1	58.5	-
II	25	"	8.0	0.0	"	49.1	-
III	60	"	8.0	0.0	"	22.5	-
IV	81	"	8.0	0.0	"	46.6	25.1[a]
I	2	June, July & Sept.	6.0	2.0	June 27	34.6	0.0
II	23	" " "	6.0	2.0	"	29.1	3.7
III	46	" " "	6.0	2.0	"	9.8	0.0
IV	79	" " "	6.0	2.0	"	17.3	0.0
I	12	" " "	8.0	3.0	"	45.7	10.4
II	38	" " "	8.0	3.0	"	65.5	0.0
III	49	" " "	8.0	3.0	"	18.9	20.4
IV	68	" " "	8.0	3.0	"	71.0	0.0
I	5	June or July	0.0	3.0	July 1	-	0.0
II	24	" " "	0.0	3.0	"	-	0.0
III	48	" " "	0.0	3.0	"	-	0.0
IV	80	" " "	0.0	3.0	"	-	0.0

a - Apparent residues in control samples. All other sample values corrected accordingly.

Extraneous peaks observed on the chromatograms did not significantly interfere with the measurement of Dacthal and 2,4-D. Residue concentrations were determined by referring to standard curves chromatographed concurrently.

Dacthal and 2,4-D (Sesone) residues found in the strawberry samples, averaged for duplicate or triplicate analyses conducted and corrected for control and percent recovery values, are shown in Table 1. The residues reported are well below the established tolerance level. Comparison of residue values for Dacthal or Sesone treatment alone with those where Dacthal and Sesone were used in combination showed very little difference.

The results of this study indicate that the use of Dacthal and Sesone in combination for the control of weeds in strawberries does not cause potentiating effects of either herbicide relative to persistence of residues in the subsequent crop.

ACKNOWLEDGMENT

This paper represents the residue analysis of a more comprehensive project involving weed control by use of combinations of herbicides. Field experimental work was conducted and directed by Drs. R. G. Hill, Jr. and E. K. Alban of OARDC. Samples for analysis were collected by Dr. Hill from the OARDC experimental plots.

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