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Levels of DCPA, MTP, TPA, and Hexachlorobenzene in Radish Roots and Tops[1]

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Abstract. **Residues of dimethyl-2,3,5,6-tetrachloroterephthalate (DCPA), monomethyl-2,3,5,6-tetrachloroterephthalate (MTP), 2,3,5,6-tetrachloroterephthalic acid (TPA) and hexachlorobenzene (HCB) were determined in tops and roots of radish (*Raphanus sativus* L.) to which the herbicide had been applied as a soil treatment for preemergence control of weeds under commercial field conditions. Residues of these compounds in the radish roots were either negligible or less than the analytical method sensitivity (0.01 ppm for all compounds except HCB which was 0.001 ppm). Much more residues of DCPA were found in the radish tops ranging from about 2 to 13 ppm. Residues of the other compounds were higher in the tops, in all instances, than in the roots. Recoveries of all the chemicals in fortified controls ranged from 70 to 100%.**

DCPA (Dacthal, chlorthal dimethyl) is a preemergence herbicide which is applied prior to or shortly after the planting of approved crops. In the environment and soil, DCPA can be degraded by attack on its ester linkages. This results in successive demethylation of DCPA to produce MTP and TPA, respectively. During the production of formulations of Dacthal, hexachlorobenzene (HCB) can be produced as a contaminant. Therefore, residue determinations on treated materials must include DCPA, MTP, TPA, and HCB.

DCPA formulations are used for preemergence applications for the control of crabgrass and other annual grasses and certain broadleaved weeds on mineral soils in vegetables, strawberries, agronomic crops, ornamentals and turf. Although tolerance levels are established at 1 to 2 ppm in many crops (3), mustard greens (5 ppm), turnip greens (5 ppm) and turnip roots (2 ppm) could be more closely compared to radish roots and tops and have higher tolerance levels than the other previously mentioned crops (3).

DCPA is not currently registered in radishes. The purpose of these experiments was to determine the residues of DCPA, MTP, TPA, and HCB in radish tops and roots when the soil was treated at different rates with DCPA under commercial field conditions.

A spray suspension of DCPA was prepared in water using Dacthal W-75 herbicide. This spray was applied preemergence immediately after planting the 'Cherry Belle' radishes with a Hudson hand sprayer equipped with an 8003 Tee Jet nozzle at 2,068.6 mm Hg with 3 rates of active ingredient, 4.84, 8.97 and 17.94 kg/ha. The chemical was applied in 330 liters/ha, and the radishes were harvested 45 days after spray application. Normally radishes are harvested 25 to 30 days after planting. However, the growing period of the crop is dependent upon the ambient temperature of the season and can extend from 25 to 60 days. The growing period for this experiment was 45 days.

The radish treatment plots were arranged in a randomized plot design with 5 beds for each rate of application. The beds were 9.1 m long by 0.9 m wide. The control beds were represented in duplicate and were separated from the treatment beds by 2 non-treated growing rows. The soil had been treated previously with DCPA during previous growing seasons for all plots at a similar rate.

The radishes were stored in a freezer at −10°C after harvest until analysis. DCPA, MTP, and TPA were extracted after lightly rinsing the radish tops and roots with tap water and cleaned up by the updated analytical procedures developed by Diamond Shamrock (5, 1). A less polar solvent, mixed pentanes, was found to be more efficient than diethyl ether in separating DCPA from the aqueous mixture (5), and isopropyl ether was used to replace diethyl ether in separating the MTP and TPA from the aqueous phase, as recommended in the Diamond Shamrock updated analytical procedure (2).

DCPA was analyzed using gas-liquid chromatography and an electron capture detector rather than with a micro-coulometric detector (2).

MTP and TPA were derivatized with 1-N-propyl-3-p-tolyltriazene (4) and analyzed by gas-liquid chromatography using a microconductance detector in the oxidative halide mode. The microconductance detector was used rather than the recommended electron capture detector because of background interference problems with the electron capture detector.

The HCB extraction, cleanup, and analysis procedures were similar to those developed by Diamond Shamrock (1).

The levels of residues in ppm of DCPA, MTP, TPA, and HCB in 'Cherry Belle' radish tops and roots are shown in Tables 1 and 2 and represent 5 replicate plots and analyses at each application rate. Hexachlorobenzene (HCB) is not biologically active as a herbicide; however, its presence in technical DCPA herbicide necessitates the study of HCB residues in those crops for which this herbicide would be used for weed control, HCB was determined in the radish tops and roots at the 8.97 and 17.94 kg/ha rate of application as well as the controls, but not at the 4.48 kg/ha rate since the residues at the 8.97 kg/ha rate in both the tops and roots were at or below the method sensitivity level of 0.001 ppm. HCB was detected at twice the rate (17.94 kg/ha) in the radish tops (0.001 to 0.010 ppm) but not in the roots, and no significant residues were detected in either the tops or roots at the lower rate (8.97 kg/ha).

Table 1. DCPA and related compound residues[z] for preemergence weed control in 'Cherry Belle' radish tops 45 days after application.

Application rate (kg/ha)	Residues[y] (ppm)			
	DCPA	MTP	TPA	HCB
0 (controls)	0.41	<0.01	<0.01	<0.001
	0.30	<0.01	<0.01	<0.001
4.48	4.4	0.01	<0.01	------
	2.2	0.06	<0.01	------
	4.6	<0.01	0.03	------
	1.9	<0.01	<0.01	------
	1.6	0.04	<0.01	------
8.97	5.9	0.09	0.03	<0.001
	7.1	0.01	<0.01	<0.001
	10.0	0.04	0.03	<0.001
	4.8	0.06	0.02	<0.001
	8.6	0.04	0.02	0.001
17.94	4.2	0.07	0.05	0.002
	12.6	0.15	0.04	0.001
	8.1	0.13	0.06	0.002
	10.8	0.01	<0.01	0.010
	11.5	0.05	<0.01	0.002

[z]Method sensitivity for DCPA, MTP and TPA, 0.01 ppm; HCB, 0.001 ppm.

[y]Recovery studies for DCPA, 0.01 ppm (80.0%), 0.05 ppm (90.0%), 0.10 ppm (100.0%), 10.0 ppm (98.1%); MTP, 0.01 ppm (70.0%), 0.05 ppm (76.0%), 0.10 ppm (75.0%); TPA, 0.01 ppm (70.0%), 0.05 ppm (74.0%), 0.10 ppm (75.0%); HCB, 0.001 ppm (80.0%), 0.0025 ppm (82.0%), 0.005 ppm (87.0%).

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Table 2. DCPA and related compound residues[z] for preemergence weed control in 'Cherry Belle' radish roots 45 days after application.

Application rate (kg/ha)	Residues[y] (ppm)			
	DCPA	MTP	TPA	HCB
0 (control)	0.02	<0.01	<0.01	<0.001
	0.05	<0.01	<0.01	<0.001
4.48	0.03	<0.01	<0.01	------
	0.04	0.02	<0.01	------
	0.01	<0.01	<0.01	------
	0.05	0.04	0.02	------
	0.03	0.01	<0.01	------
8.97	0.04	0.01	0.01	<0.001
	0.02	0.06	<0.01	<0.001
	0.02	<0.01	0.03	<0.001
	0.01	<0.01	<0.01	<0.001
	0.03	<0.01	<0.01	<0.001
17.94	0.12	0.01	0.01	<0.001
	0.12	0.01	<0.01	0.001
	0.11	0.05	0.02	<0.001
	0.22	0.03	0.01	<0.001
	0.07	<0.01	<0.01	<0.001

[z]Method sensitivity for DCPA, MTP and TPA, 0.01 ppm; HCB, 0.001 ppm.

[y]Recovery studies for DCPA, 0.01 ppm (90.0%), 0.05 ppm (98.0%), 0.10 ppm (99.0%); MTP, 0.01 ppm (70.0%), 0.05 ppm (74.0%), 0.10 ppm (75.0%). TPA, 0.01 ppm (70.0%), 0.05 ppm (76.0%), 0.10 ppm (75.0%); HCB, 0.001 ppm (80.0%), 0.0025 ppm (88.0%), 0.005 ppm (80.0%).

The levels of DCPA residues in the radish roots ranged at the 4.48 kg/ha rate from 0.01 to 0.05 ppm, at the 8.97 kg/ha rate from 0.01 to 0.04 ppm, and the 17.94 kg/ha rate from 0.07 to 0.22 ppm. The controls had 0.02 to 0.05 ppm apparent residue which was determined by gas-liquid chromatography coupled to a mass spectrometer to be DCPA. The levels of MTP and TPA in the radish roots ranged from <0.01 to 0.04 and <0.01 to 0.02 ppm at the 4.48 kg/ha rate; <0.01 to 0.06 and <0.01 to 0.03 at the 8.97 kg/ha rate; and <0.01 to 0.05 and <0.01 to 0.02 at the 17.94 kg/ha rate (Table 2).

The levels of residues in the radish tops for DCPA ranged at the 4.48 kg/ha rate from 1.6 to 4.6 ppm; at the 8.97 kg/ha rate from 4.8 to 10.0 ppm; and the 17.94 kg/ha rate from 4.2 to 12.6 ppm. The controls had 0.30 to 0.41 ppm apparent residue which was determined by gas-liquid chromatography coupled to a mass spectrometer to be DCPA. The levels of MTP and TPA in the radish tops ranged from <0.01 to 0.06 and <0.01 to 0.03 ppm at the 4.48 kg/ha rate; 0.01 to 0.09 and <0.01 to 0.03 ppm at the 8.97 kg/ha rate; and 0.01 to 0.15 and <0.01 to 0.06 ppm at the 17.94 kg/ha rate (Table 1).

Residues of DCPA, MTP, TPA and HCB in radishes were detected in significant amounts in the tops, and only trace amounts were present in the roots under treatment conditions of this experiment.

Literature Cited

1. Anon. 1970. Pesticide analytical methods, Vol. II. Pesticide Reg. Sec. 120.185, Methods A and B. U.S. Dept. of Health, Educ., & Welfare, Food & Drug Admin.
2. Ballee, D. L. and D. E. Stallard. 1975. Dacthal. Diamond Shamrock, T. R. Evans Res. Center, Painesville, Ohio.
3. Environmental Protection Agency. 1969. EPA Compendium of Registered Pesticides. I-D-67.2. Washington, D.C.
4. Mason, G. and D. J. Lisk. 1978. Residues of dacthal herbicide in carrots. *Bul. Environ. Contam. Toxicol.* 20:180-183.
5. Miller, F. M. and E. D. Gomes. 1974. Detection of DCPA residues in environmental samples. *Pesticide Monitoring J.* 8(1):53-58.

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Glycoalkaloids of Hollow Heart and Blackheart Potato Tubers[1,2]

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Abstract. **Tubers of potato (*Solanum tuberosum* L.) with the nonparasitic disorders of hollow heart and blackheart contained significantly more glycoalkaloids in the cortical region than normal tubers in 3 cultivars. The glycoalkaloid content of tuber tissue was related to the severity of the disorders.**

The glycoalkaloids naturally occurring in potato tubers have been associated with bitter taste, objectionable off-flavor, inhibition of cholinesterase, and poisoning in humans and animals. The level of glycoalkaloids in the tubers depends upon cultivar, state of development, and nature of storage or growth environment. Light and mechanical injury are the most well known factors which stimulate glycoalkaloid synthesis in the potato tubers (3, 7, 9, 13).

Hollow heart and blackheart are very common nonparasitic disorders of potatoes grown anywhere in the world. The former has its inception in the field (1, 4, 5, 6) while the latter develops during shipment or storage (2, 11). The effect of these disorders on glycoalkaloid content has not been reported. This investigation was undertaken to determine the extent of the effect of these disorders on glycoalkaloids of potato tubers.

'Russet Burbank', 'Norgold Russet', and 'Pontiac' tubers were obtained from local potato growers who suspected hollow heart and blackheart disorders. Tubers of 250 ± 10 g were selected for screening and cut in half from basal to apical end. Halves with slight and severe hollow heart and blackheart symptoms were chosen by visual observation. Since the glycoalkaloid concentration is arranged in an ascending gradient from the inside outward, the potato halves were sampled by cutting longitudinal portions only 1 cm away from the periderm. A control sample was similarly prepared from normal tubers for comparison. Triplicate samples on each treatment were freeze-dehydrated for total glycoalkaloid determination and triplicate analyses were conducted on each sample amounting to 50 g. The Gull and Isenberg method (3) was followed for glycoalkaloid determination. It involved Soxhlet extraction, liquid ammonia precipitation, followed by color development and spectrophotometric quantitation. The procedure for color development required drop by drop addition of 5 ml of concentrated sulfuric acid to an aliquot of glycoalkaloids over a period of exactly 3 minutes, followed by like addition of 2.5 ml of 1% formaldehyde over a period of exactly 2 minutes. This was accomplished by using a constant volume burettes mounted on an automatic shaking device (14). Glycoalkaloid content was expressed as milligrams per 100 gram dry tissue. Analysis of variance was made and means were compared according to Tukey w-procedure (10).

Potato tubers with the nonparasitic disorders of hollow heart and blackheart contained significantly more glycoalkaloids than normal tubers. This phenomenon was consistently shown by 3 cultivars of potatoes tested (Table 1).

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