ty of response thus obtained in the range 0.05–10 ng for CT and EDB and in the range 1.5–40 ng for EDC was similar to that obtained with 100% acetone. Reproducibility of response was better with 100% acetone as the extraction solvent, which became the solvent of choice for extraction of cereal samples.

Recoveries by the method of standard addition by which amounts of 1–1000 μg of fumigant in standard solutions were added to acetone extracts of untreated wheat to a total volume of 10 ml showed that amounts ranging from 0.1 to 40 ng of CT and EDB and from 1.5 to 100 ng of EDC could be measured with 95–100% recovery by EC detection.

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Endosulfan Persistence in Soil and Uptake by Potato Tubers

Donald K. R. Stewart* and Kenneth G. Cairns

Studies on technical endosulfan incorporated into soil at a rate of 6.7 kg/ha showed that α-endosulfan decomposed fairly rapidly (50% in ~60 days) with the simultaneous formation of equivalent amounts of endosulfan sulfate which appeared to be relatively stable in soil. β-Endosulfan disappeared slowly (~50% in 800 days). Residues in potato tubers due to direct absorption from the soil, in the same season that endosulfan was applied at 6.7 kg/ha, were 0.3 ppm of endosulfan sulfate, 0.06 ppm of β-endosulfan, and 0.01 ppm of α-endosulfan in peel and 0.03 ppm of endosulfan sulfate in pulp. Eight foliar sprays, each applied at the rate of 0.6 kg/ha, resulted in residues of 0.01 ppm of endosulfan sulfate in peel and pulp.

Endosulfan (6,7,8,9,10,10-hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzodioxathiepin 3-oxide) is recommended as an insecticide on a number of crops in Nova Scotia and repeated sprays may be applied each season depending on the crop and insect involved. Since endosulfan has been in use for more than 15 years a considerable amount of information is available on residues in plants and metabolism in animals (Maier-Bode, 1968). However, there does not appear to be any information in the literature dealing specifically with the persistence of endosulfan in soil.

The present study reports the persistence of technical endosulfan in sandy loam soil, the direct absorption from soil by potato tubers, and the tuber residues resulting from repeated foliar sprays of endosulfan.

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MATERIALS AND METHODS

Soil Treatments. Four plots (7 × 5 m) were established July 28, 1970 on a Somerset sandy loam (Cann *et al.*,

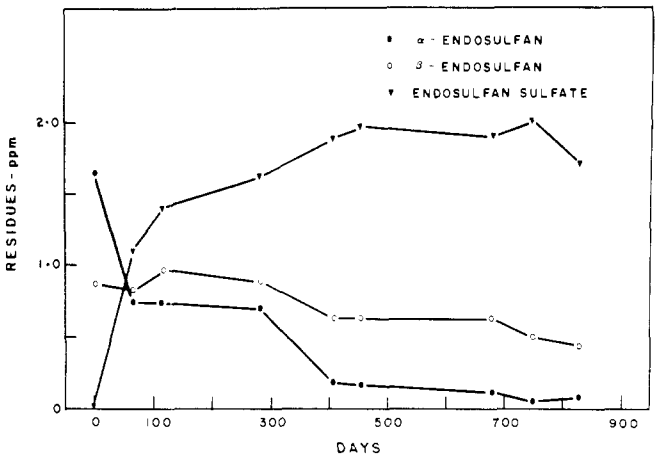

Figure 1. Residues of α-endosulfan, β-endosulfan, and endosulfan sulfate in soil resulting from incorporation of 6.7 kg/ha of endosulfan on July 28, 1970.

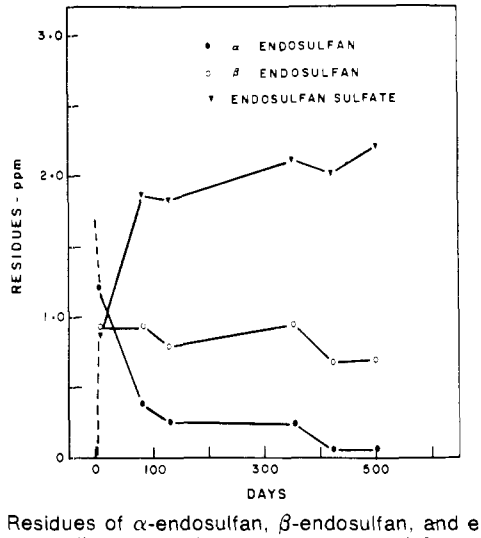

Figure 2. Residues of α-endosulfan, β-endosulfan, and endosulfan sulfate in soil resulting from incorporation of 6.7 kg/ha of endosulfan on June 18, 1971.

1965) containing 68% sand, 20% silt, and 12% clay in a randomized pesticide block consisting of 40 plots. Four additional plots were established in the same block June 18, 1971. Technical endosulfan (Thiodan 2E, FMC Corporation) was applied at a rate of 6.7 kg/ha by spraying the surface of the plots with an aqueous emulsion and incorporating it into the soil to a 15-cm depth with a rotovator.

Soil Sampling. The plots established July 28, 1970 were sampled at 1, 64, 114, 283, 408, 454, 679, 751, and 828 days. At each date a composite sample of 10 soil cores was taken from each plot; in 1970 the 0–15-cm depth was sampled and in 1971 and 1972 the 0–15-, 15–30-, and 30–45-cm depths. Samples from each plot were air-dried at room temperature, screened through a 2-mm sieve, and stored at 1°. The plots established on June 18, 1971 were sampled at 5, 83, 129, 354, 426, and 503 days. On all these dates the 0–15-, 15–30-, and 30–45-cm depths were sampled.

Foliar Sprays. A single plot (21 × 5 m) was established in 1971. Three rows of potatoes, cultivar Kennebec, were planted June 18, 1971 and sprays of endosulfan (Thiodan 2E) applied at a rate of 0.6 kg/ha on July 26, Aug 3, 10, 17, 24, 31, and Sept 9 and 15. Tops were cut on Sept 30 and tubers harvested Oct 12. Dithane M-45, 80% WP (Rohm & Haas), was applied six times at a rate of 1.1 kg/ha to control potato blight. A derris formulation was applied as needed to control potato beetle, *Leptinotarsa decemlineata* (Say). In 1972 a similar experiment was carried out. Potatoes were planted June 26 and sprayed with Thiodan 2E on July 24, 31, Aug 7, 14, 22, 30, and Sept 6 and 13. Tops were cut Oct 5 and tubers harvested Oct 16. Dithane M-45 was applied nine times during the season.

Residue Absorption by Tubers. Potatoes were grown on portions of the plots established in 1970 and 1971 for soil persistence studies according to the following scheme.

	Potatoes grown		
Plots estbld	1970	1971	1972
1970	No crop	4 plots	2 plots
1971		4 plots	2 plots

Potatoes were planted and harvested on the same dates as those in the previously described foliar residue experiment. Dithane was applied on the same dates also.

Crop Sampling. Representative tuber samples from each plot were given a cold water wash with a soft brush to remove adhering soil particles. The samples were divided into peel and pulp and diced, and several 100-g subsamples of each were frozen in plastic bags and stored at −20° until analyzed. The peel comprised approximately 15% of the weight of the tuber.

Extraction of Residues. Residues were extracted from 10.0-g soil samples with 350 ml of hexane–acetone (1:1, v/v) in Soxhlet extractors for 4 hr. The extraction thimble was Pyrex glass, 90 mm long × 35 mm diameter, with an "Extra coarse" fritted glass disk. A glass fiber filter paper 37 mm in diameter was placed on the disk, then a layer of

Table I. Residues in Potato Tubers Grown in Soil Treated with Endosulfan at 6.7 kg/ha

		Residues, ppm		
Endosulfan applied	Sample	α-Endosulfan	β-Endosulfan	Endosulfan sulfate
1970	1971[a] Peel	Tr[c]	0.02	0.15
	Pulp	N.D.[d]	N.D.	0.02
	1972[b] Peel	Tr	Tr	0.05
	Pulp	N.D.	N.D.	0.01
1971	1971[a] Peel	0.01	0.06	0.30
	Pulp	N.D.	N.D.	0.03
	1972[b] Peel	Tr	0.01	0.10
	Pulp	N.D.	N.D.	0.01

[a] Each value is the mean of four replicates. [b] Each value is the mean of two replicates. [c] Trace, detected at level <0.01 ppm. [d] N.D., not detected; sensitivity of method ~ 0.005 ppm.

Table II. Residues in Potato Tubers Due to Eight Foliar Sprays of Endosulfan at 0.6 kg/ha

Endosulfan applied		Residues, ppm		
		α-Endosulfan	β-Endosulfan	Endosulfan sulfate
1971	Peel	Tr	N.D.	0.01
	Pulp	N.D.	N.D.	0.01
1972	Peel	Tr	Tr	0.01
	Pulp	N.D.	N.D.	0.01

[a] Each value is the mean of two replicates.

3-mm glass beads, followed by the soil sample moistened with 1 ml of water, followed by a small pad of Pyrex glass wool. Extracts were evaporated to dryness on a rotary evaporator at 40° and the residue dissolved in 10 ml of hexane–acetone (1:1) and refrigerated until analyzed.

A 100-g frozen potato peel or pulp sample was placed in a blender jar, 200 ml of pesticide grade acetonitrile was added, and, after thawing, the sample was blended for 2 min with a Virtis homogenizer. The homogenate was filtered on a Büchner funnel, and the precipitate reextracted, refiltered, and washed on the funnel with acetonitrile. The total filtrate was concentrated to about 200 ml with a rotary evaporator, added to a 2-l. separatory funnel together with 1400 ml of water and 25 g of NaCl, and extracted with 100 ml of hexane. The extraction was repeated twice and the total hexane extracts dried by passing through a column of anhydrous sodium sulfate. The extracts were concentrated to a 10-ml volume and refrigerated until cleanup.

Cleanup of Potato Extracts. The concentrated hexane extract above was divided into two portions. For the determination of α-endosulfan one was cleaned up on a 21-mm diameter column containing 21 g of pesticide grade Florisil which had been activated 1 hr at 130°. The α-endosulfan was eluted with 200 ml of hexane containing 30% ether. The second portion of the extract was used for the determination of β-endosulfan and endosulfan sulfate and was more conveniently cleaned up by partitioning between hexane and acetonitrile.

Recoveries of α- and β-endosulfan and endosulfan sulfate from potato peel and pulp samples spiked at the 0.2-ppm level ranged from 90 to 100% using the above extraction and cleanup methods.

Residue Determinations. Residues of α- and β-endosulfan and endosulfan sulfate were determined by gas chromatography using a Micro Tek 220 with a ^{63}Ni electron capture detector operated in the pulse mode. The column was 122 cm × 0.64 cm Pyrex glass packed with 3% OV-17 on Gas Chrom Q, 100–120 mesh. Carrier gas was argon, containing 5% methane, at a flow rate of 85 cm^3/min. The oven temperature was 195° and the detector temperature 275°. The pulse rate was 270 μsec and the pulse width 3 μsec. Retention times were 6.9, 13.3, and 19.5 min for α-endosulfan, β-endosulfan, and endosulfan sulfate, respectively.

Standard curves were prepared several times daily by plotting peak heights *vs.* amount of insecticide injected.

RESULTS AND DISCUSSION

The technical endosulfan applied to the soil contained the α and β isomers in the ratio 2:1. The α isomer decomposed relatively rapidly in the plots established in 1970, about 50% having disappeared in 60 days with the simultaneous appearance of an equivalent amount of endosulfan sulfate (Figure 1) which was identified by its retention time on three gas chromatographic columns and by thin-layer chromatography on alumina with the solvent system acetone–hexane (1:6). β-Endosulfan disappeared more slowly; approximately 800 days were needed for 50% to disappear. The persistence of soil residues in plots established in 1971 followed the same general trend (Figure 2) as in the 1970 plots. α-Endosulfan disappeared somewhat more rapidly (~50% in 40 days) with a proportionately more rapid rate of formation of endosulfan sulfate. The total loss of the α and β isomers was approximately equal to the endosulfan sulfate formed (Figures 1 and 2). This suggests that the two isomers are quantitatively converted to the sulfate which appeared to be relatively stable in soil during the experiment. This stability is of interest in view of the approximately equal toxicities of the α and β isomers and the sulfate to insects (Barnes and Ware, 1965). The difference in the stabilities of the two isomers in soil must be related in some way to their stereochemistry. The analysis of soil samples representative of the three depths showed an average of 90% of the residues to be in the 0–15-cm depth, 9% in the 15–30-cm depth, and 1% in the 30–45-cm depth. The per cent distribution with depth remained relatively constant throughout the study. For simplicity the total residues of each of α-endosulfan, β-endosulfan, and endosulfan sulfate in the 0–45-cm depth were expressed as if they were all contained in the 0–15 cm (6 in.) depth and are plotted in Figures 1 and 2.

Soil residues resulting from foliar sprays applied to potatoes were small and confined to the 0–4-cm depth of the soil. Residues of 0.1 ppm of α-endosulfan, 0.1 ppm of β-endosulfan, and 0.08 ppm of endosulfan sulfate were found in the 0–15-cm depth at harvest Oct 16, 1972 following eight foliar sprays, each of 0.6 kg/ha, applied from July 24 to Sept 13.

Endosulfan residues in potato tubers due to direct absorption from soil are presented in Table I. The highest residues were found in the peel in the same year endosulfan was applied. In the second and third seasons after application the residues were less and consisted almost entirely of endosulfan sulfate in peel and pulp. No α or β isomers were found in pulp in any season.

In the third season after endosulfan application when the endosulfan sulfate concentration in soil was highest (Figure 1) its concentration in peel was lowest (Table I). It appears probable that endosulfan sulfate in tuber peel arises from conversion of the α and β isomers in the tissue.

Endosulfan residues in tubers resulting from eight foliar sprays in 1971 and 1972 were very small (Table II) consisting almost entirely of endosulfan sulfate at 0.01 ppm in peel and pulp. This is near the detection limit of the analytical method. These residues may be due to translocation from the foliage but since they are so minute it is possible they resulted from contamination by soil during harvesting.

The results of the present study indicate that β-endosulfan and endosulfan sulfate are relatively persistent in soil and although the direct absorption of these residues from soil by potatoes is small, other crops, such as carrots, might accumulate significant amounts.

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