DYNAMAC
CORPORATION

ENDOSULFAN ADDENDUM

Final Report

Task 1: Review and Evaluation of Individual Studies

Contract No. 68-01-6679

SEPTEMBER 19, 1985

Submitted to:
Environmental Protection Agency
Arlington, VA 22202

Submitted by:
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Enviro Control Division
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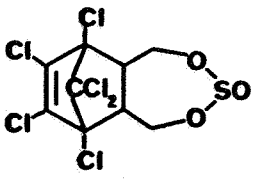
ENDOSULFAN

BEOSIT, CHLORTHIEPIN, CRISULFAN, CYCLODAN, DEVISULPHAN, ENDOCEL, ENDOSOL, ENSURE, FMC 5462, HILDAN, HOEFAN, THIFOR, THIMUL, THIODAN, THIOFOR, THIONEX, THIOSULFAN, TIOVEL



6,7,8,9,10,10-Hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzodioxathiepin-3-oxide

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CASE GS0014 ENDOSULFAN STUDY 1 PM 110 08/12/79

CHEM 079401 Endosulfan

BRANCH EFB DISC --

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID No MRID CONTENT CAT 01

Gildemeister, H. and H. J. Jordan. 1984. Aerobic soil metabolism study of the insecticide Hoe 002671 (Endosulfan). In Endosulfan reregistration: November 1984 data requirements; Thiodan technical. Unpublished study received January 9, 1985 under 8340-13; submitted by American Hoechst Corporation, Somerville, NJ. Accession No. 256130.

SUBST. CLASS = S.

DIRECT RVW TIME = 4 (MH) START-DATE END DATE

REVIEWED BY: S. Hathorn III
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SIGNATURE: S. Hathorn III DATE: Aug. 13, 1985

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CONCLUSIONS:

Metabolism - Aerobic Soil

1. This study is scientificaly valid.

2. 5a,9a-Labeled [^{14}C]endosulfan (97.0% pure) at ~3.5 ppm degraded with half-lives of 4-8 and 16-30 days in sandy loam and silt loam soils, respectively. Degradates common to both soils included endosulfan-sulfate, endosulfan lacton and an unidentified degradate, M4, at respective levels of <45%, 0.2-1.0% and 1.1-4.8%. The ether degradate was found at ~0.02 ppm in two samples of the silt loam soil. Total recovered volatiles were <4% of the applied.

3. This study does not fulfill EPA Data Requirements for Registering Pesticides because the soil moisture content was not maintained at 75% of 0.33 bar, several degradates occurring at >0.01 ppm were not identified, and the pattern of formation and decline of endosulfan-sulfate was not established because the test period was too short.

MATERIALS AND METHODS:

5a,9a-Labeled [^{14}C]endosulfan (specific activity 1.0 mCi/g, radiochemical purity 97.0%, Hoechst AG), as an alpha:beta [redacted] isomeric mixture, was mixed at ~3.5 ppm in methylene chloride with previously sieved (1 mm) sandy loam and silt loam soils (Table 1). One flask of each soil was attached to a closed aeration system (Figure 1), which was purged daily for eight hours to flush and trap volatiles. The trapping system included ethanolamine:methanol (3:7) for $^{14}CO_2$, and sulfuric acid and ethylene glycol for other volatile degradates. These and the other incubation flasks, which were sealed with cotton-wool plugs, were maintained at 40% of 0.33 bar moisture content during incubation in darkness at 22 ± 2 C. Test soils were sampled 0, 1, 2, 4, 8, 16, 30, and 60 days posttreatment. The volatile trap solutions were sampled on days 8, 16, 30, and 60.

The soils were extracted with acetonitrile:toluene (80:20) then combusted for LSC analysis of unextractable residues. Soil extracts and volatile trap solutions were also counted by LSC. Concentrated soil extracts were analyzed by HPLC equipped with a radioactivity monitor with degradate identification by comparison to a HPLC chromatogram of known degradates.

REPORTED RESULTS:

5a,9a-Labeled [^{14}C]endosulfan at ~3.5 ppm degraded aerobically in sandy loam and silt loam soils with calculated half-lives of 18 and 27 days, respectively, based on first-order kinetics. Endosulfan-sulfate was the major degradate in both soils and gradually increased to as much as ~45% of the applied in the sandy loam soil (Tables 2 and 3). Endosulfan-lacton was found in both soils at 0.2-1.0% of the applied, while the ether degradate was 0.8% (~0.02 ppm) of the applied in the silt loam soil. Degradate M4 was also detected in both soils at 1.1-4.8% (~0.03-0.14 ppm) of the applied. Degradates M6, M7 and M8 were found at concentrations of ~0.02 ppm in various samples. Only 1.8 and 2.8%, respectively, of the applied was evolved as $^{14}CO_2$ from the silt loam and sandy loam soils (Table 4). Volatiles from the sulfuric acid plus ethylene glycol traps were 1.2-1.8% of the applied.

DISCUSSION:

1. The soil moisture content was not maintained at 75% of 0.33 bar during incubation.

2. Analytical recoveries and limits of detection for the GC method were not reported.

3. Degradates M4, M6, M7, and M8, which occurred at concentrations >0.01 ppm, were not identified.

4. The pattern of formation and decline of endosulfan-sulfate was not clearly established within the test period (60 days).

5. The test soil reported as a loamy sand is a sandy loam according to the USDA soil textural classification system.

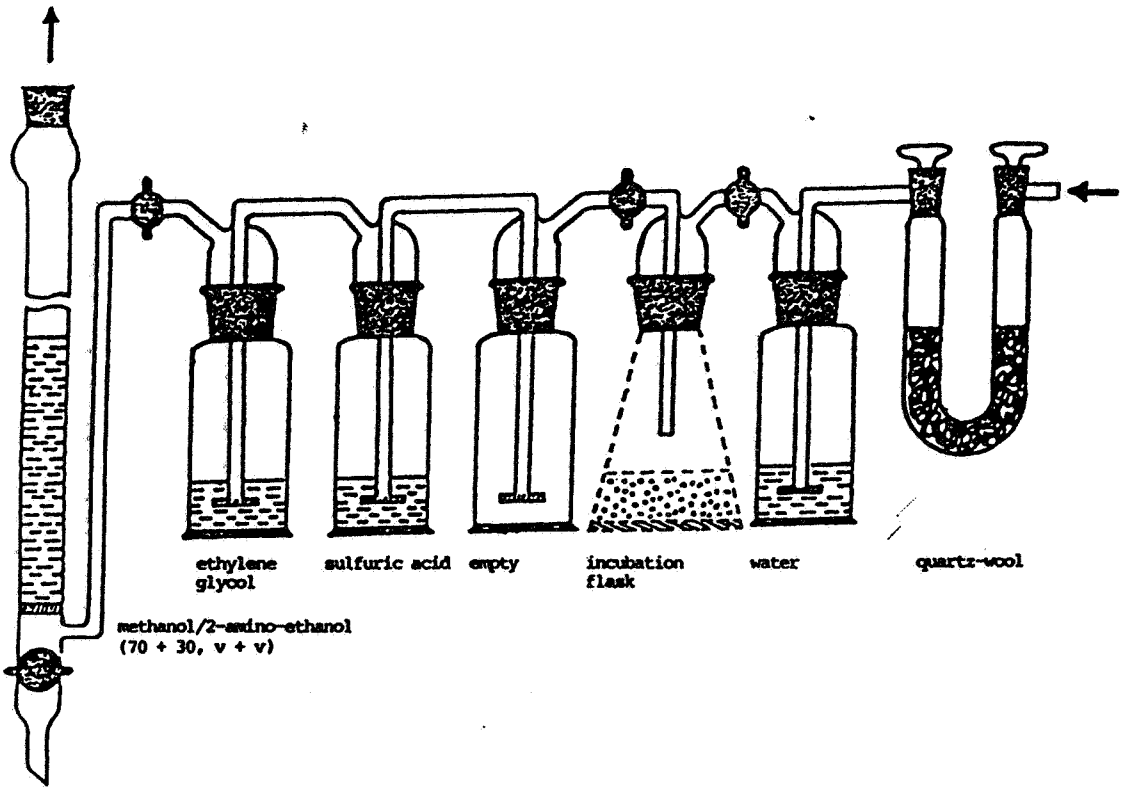

Figure 1. Closed aeration system.

Table 1. Soil characteristics.

Soil type	Source	Sand	Silt	Clay	Organic matter	CEC (meq/100 g)	pH
		%					
Sandy loam[a]	Germany	63.0	31.6	5.4	2.7	2.9	4.7
Silt loam	MS, USA	7.2	70.4	22.4	1.6	21.3	6.4

[a] Reported as a loamy sand; see Discussion No. 5.

Table 2. Radioactivity (% of applied) in soils treated with 5a,9a-labeled [^{14}C]endosulfan at ~3.5 ppm and aerobically incubated in darkness at ~22 C.

Sampling interval (days)	Extractable	Unextractable	Total recovered
		Sandy loam	
0	94.7	5.0	99.7
1	88.8	10.1	98.9
2	74.9	16.2	91.1
4	75.6	16.2	91.8
8	72.8	24.9	97.7
16	83.3	11.2	94.5
30	75.4	2.7	78.1
60	70.0	26.3	96.3
		Silt loam	
0	83.7	8.7	92.4
1	76.3	22.2	98.5
2	82.6	20.4	103.0
4	81.7	18.8	100.5
8	69.1	25.5	94.6
16	79.0	20.0	99.0
30	53.7	2.3	56.0
60	39.2	45.2	84.4

Table 3. Distribution of radioactivity (% of applied) in soils treated with 5a,9a-labeled [^{14}C]endosulfan at ~3.5 ppm and aerobically incubated in darkness at ~22 C.

Sampling interval (days)	α-E[a]	β-E[b]	M1[c]	M2[d]	M3[e]	M4	M5	M6	M7	M8
				Sandy loam						
0	62.2	32.5	--	--	--	--	--	--	--	--
1	63.8	21.9	3.1	--	--	--	--	--	--	--
2	42.8	20.2	11.8	--	--	--	--	--	--	--
4	36.5	19.8	19.4	--	--	--	--	--	--	--
8	26.9	19.4	26.1	0.2	--	--	--	--	--	--
16	17.1	21.0	44.6	0.6	--	--	--	--	--	--
30	8.3	16.8	45.1	0.6	--	3.1	--	0.6	0.9	--
60	3.6	25.7	38.6	0.8	--	1.3	--	--	--	--
				Silt loam						
0	56.2	27.5	--	--	--	--	--	--	--	--
1	54.0	20.2	2.0	--	--	--	--	--	--	--
2	60.2	21.8	0.5	--	--	--	--	--	--	--
4	57.5	22.6	1.5	--	--	--	--	--	--	--
8	44.5	19.4	3.9	--	0.8	--	0.2	--	--	--
16	49.5	20.1	9.3	--	--	--	--	--	--	--
30	19.8	20.4	10.0	1.0	0.8	1.1	--	--	--	0.6
60	3.2	12.6	18.6	--	--	4.8	--	--	--	--

[a] Alpha-endosulfan isomer.

[b] Beta-endosulfan isomer.

[c] Endosulfan-sulfate.

[d] Endosulfan-lacton.

[e] Endosulfan-ether.

Table 4. Radioactivity (% of applied) in volatile traps evolved from soils treated with 5a,9a-labeled [^{14}C]endosulfan at ~3.5 ppm and aerobically incubated in darkness at ~22 C in a closed system.

Soil type	Sampling interval (days)	Sulfuric acid	Ethylene glycol	Ethanolamine: methanol	Total volatiles
Loamy sand	8	0.3	0.2	0.3	0.8
	16	0.1	0.2	0.3	0.6
	30	0.4	0.5	1.0	1.9
	60	--	0.1	0.2	0.3
Silt loam	8	0.2	0.1	0.3	0.6
	16	--	0.2	0.2	0.4
	30	0.2	0.3	1.2	1.7
	60	0.1	0.1	1.1	1.3

CASE GS0014 ENDOSULFAN STUDY 2 PM 110 08/12/79

CHEM 079401 Endosulfan

BRANCH EFB DISC --

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID No MRID CONTENT CAT 01

Gildemeister, H. 1985. Anaerobic soil metabolism study with the insecticide endosulfan. In Endosulfan reregistration: Thiodan technical. Unpublished study received April 19, 1985 under 8340-13; submitted by American Hoechst Corporation, Somerville, NJ. Accession No. 257688.

SUBST. CLASS = S.

DIRECT RVW TIME = 4 (MH) START-DATE END DATE

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CONCLUSION:

Metabolism - Anaerobic Soil

This study is scientifically invalid because the material balances were unacceptably variable and low. Additionally, this study would not fulfill EPA Data Requirements for Registering Pesticides because the isomeric ratio of the test substance was not reported, and several degradates occurring at >0.01 ppm were not identified.

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MATERIALS AND METHODS:

5a,9a-Labeled [^{14}C]endosulfan (specific activity 1.0 mCi/g, radiochemical purity 97.0%, Hoechst AG), as an alpha:beta (ratio unspecified) isomeric mixture was mixed at ~3.2 ppm in methylene chloride with previously sieved (1 mm) loamy sand and silt loam soils (Table 1) in flasks. The flasks were sealed with cotton-wool plugs and maintained at 40% of 0.33 bar moisture content during aerobic incubation in darkness at 22 ± 2 C. After 30 days of aerobic incubation, the soils were converted to anaerobic conditions by flooding with distilled water and flushing with nitrogen. Just before conversion to anaerobic conditions, 10 mg of peptone, a substrate for anaerobic metabolism, was added to each treated soil. The flasks were then sealed with glass stoppers and stored in darkness at 22 ± 2 C. Soils were sampled at 0, and 30 days posttreatment (aerobic conditions), and at 15, 30, 44 and 61 days after establishing anaerobic conditions.

The soils were extracted with acetonitrile:toluene (80:20) then combusted for LSC analysis of unextractable residues. Concentrated soil extracts were analyzed by LSC and by HPLC equipped with a radioactivity monitor. Degradates were identified by comparison to a HPLC chromatogram of known degradate standards.

REPORTED RESULTS:

Total extractable ^{14}C (LSC) and concentrations of 5a,9a-labeled [^{14}C]endosulfan (alpha plus beta isomers) decreased in both soils during aerobiosis and continued to do so through the 30-day anaerobic sampling, then increased during the 30-44 day anaerobic interval, then diminished again during the final sampling interval (Tables 2 and 3). Endosulfan-sulfate, the major degradate, followed the inverse pattern in the silt loam soil and, to a lesser extent, in the loamy sand. The apparent reversion of endosulfan-sulfate to endosulfan was attributed to a reducing effect upon the sulfate group under anaerobic conditions. Endosulfan-ether at concentrations up to 0.02 ppm was detected in the silt loam but was not found in the loamy sand soil. Other unidentified degradates, including M1, M2, M3, M6, M7, M9, M10, and M11, were detected at ~0.01-0.08 ppm in various samplings of one or both soils.

DISCUSSION:

1. The isomeric ratio of the test substance was not reported.

2. The test soil reported as a silty sand is a loamy sand according to the USDA soil textural classification system.

3. Analytical recovery values and limits of detection for the GC method were not provided.

4. The mass balances for extractable and unextractable soil ^{14}C were unacceptably variable (36.9-99.7% of applied) and low (36.9 and 56.0%). Additionally, the radioactivity in the anaerobic incubation water layers was not quantified or characterized.

5. Several degradates (M1, M2, M3, M6, M7, M9, M10, M11), which occurred at >0.01 ppm, were not identified.

Table 1. Soil characteristics.

Soil type	Source	Sand	Silt	Clay	Organic matter	CEC (meq/100 g)	pH
		%					
Loamy sand[a]	Germany	77.5	19.9	2.6	1.8	2.9	4.1
Silt loam	MS USA	7.2	70.4	22.4	1.6	21.3	6.4

[a] Reported as a silty sand; see Discussion No. 2.

Table 2. Radioactivity (% of applied) in soil treated with 5a,9a-labeled [^{14}C]endosulfan at ~3.2 ppm and anaerobically incubated in darkness at ~22 C.

Sampling interval (days)		Extractable	Unextractable	Total recovered
			Loamy sand	
- 30	(aerobic)	94.7	5.0	99.7
0	(anaerobic)	75.4	2.7	78.1
15		58.4	12.0	70.4
30		25.0	11.9	36.9
44		83.0	8.1	91.1
61		64.6	11.7	76.3
			Silt loam	
- 30	(aerobic)	83.7	8.7	92.4
0	(anaerobic)	53.7	2.3	56.0
15		61.3	14.6	75.9
30		74.0	7.3	81.3
44		84.1	2.6	86.7
61		68.8	4.8	73.6

Table 3. Distribution of radioactivity (% of applied) in soils treated with 5a,9a-labeled [^{14}C]endosulfan at ~3.2 ppm and anaerobically incubated in darkness at ~22 C.

Sampling interval (days)	α-E[a]	β-E[b]	M1	M2	M3	M4[c]	M5[d]	M6	M7	M8[e]	M9	M10	M11
Loamy sand													
-30 (aerobic)	62.2	32.5	--	--	--	--	--	--	--	--	--	--	--
0 (anaerobic)	8.3	16.8	--	3.1	0.6	0.6	45.1	0.9	--	--	--	--	--
15	1.7	3.1	--	1.7	--	--	51.7	--	--	--	--	--	--
30	0.2	3.8	--	3.1	--	--	17.6	--	--	--	--	--	--
44	13.0	15.5	--	1.6	--	--	52.7	--	--	--	--	--	--
61	7.2	10.8	0.5	3.2	--	2.8	34.1	--	2.7	--	1.3	--	0.6
Silt loam													
-30 (aerobic)	56.2	27.5	--	--	--	--	--	--	--	--	--	--	--
0 (anaerobic)	19.8	20.4	--	1.1	--	1.0	10.0	--	0.6	0.8	--	--	--
15	14.5	9.8	--	0.7	--	--	36.0	--	--	--	--	--	--
30	3.2	1.3	--	1.4	--	--	67.8	--	--	--	--	--	--
44	41.3	22.8	--	2.1	--	--	16.3	--	--	0.1	--	1.0	--
61	27.1	18.9	--	0.6	--	--	22.0	--	--	--	--	--	--

[a] Alpha-endosulfan isomer.

[b] Beta-endosulfan isomer.

[c] Endosulfan-lacton.

[d] Endosulfan-sulfate.

[e] Endosulfan-ether.

CASE GS0014 ENDOSULFAN STUDY 3 PM 110 08/12/79

CHEM 079401 Endosulfan

BRANCH EFB DISC --

FORMULATION --

FICHE/MASTER ID No MRID CONTENT CAT 01

Gorlitz G., and C. Klockner. 1982. Hydrolysis of HOE 02671 (endosulfan). Unpublished study received May 30, 1983 under 8340-13. Submitted by American Hoechst Corporation, Somerville, NJ. Accession No. 250395.

SUBST. CLASS = S.

DIRECT RVW TIME = (MH) START-DATE END DATE

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CONCLUSION:

Mobility - Laboratory Volatility

The vapor pressure for α- and β-endosulfan at 295 K has been reported as 1.2×10^{-5} mbar and 0.56×10^{-6} mbar, respectively. This study does not fulfill EPA Data Requirements for Registering Pesticides because no experimental data were provided to allow an assessment of endosulfan volatility.