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ORIGINAL SIGNED BY
HUDSON L. BOYD

DICROTOPHOS

Task 1: Review and Evaluation of Individual Studies

Contract No. 68-01-5830

Final Report

October 7, 1981

SUBMITTED TO:

Environmental Protection Agency
Arlington, Virginia 22202

SUBMITTED BY:

Enviro Control, Inc.
The Dynamac Building
11140 Rockville Pike
Rockville, MD 20852

A Subsidiary of the Dynamac Corporation

DICROTOPHOS

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DICROTOPHOS

Table of Contents

CASE GS0035 DICROTOPHOS STUDY 1 FF 12/03/80

CHEM 035201

BRANCH EFB DISC 30 TOPIC 051515 GUIDELINE 40 CFR 163.62-7c

FORMULATION 90 - FORMULATION NOT IDENTIFIED

FICHE/MASTER ID 00028576 CONTENT CAT 01

Hall, W.E.; Saliman, P.M. (1983) Sunlamp Stability of SD 9129 and Bidrin¬(R)¤ Insecticide. (Unpublished study received Mar 18, 1980 under 6F1851; submitted by Shell Chemical Co., Washington, D.C.; CDL:099341-F)

SUBST. CLASS = S.

DIRECT REV TIME = 6½ (MH) START-DATE END DATE

REVIEWED BY: W. Hazel
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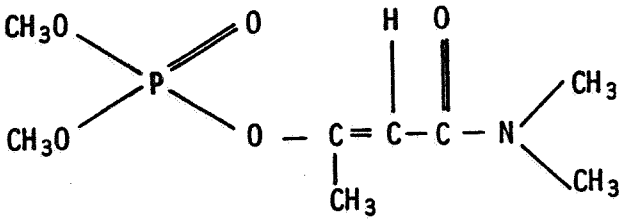
CONCLUSION:

Degradation - Photodegradation in Water

This study is scientifically invalid because the methods were incompletely presented and because appropriate controls were not included.

MATERIALS AND METHODS:

DICROTOPHOS, BIDRIN, C 709, CARBICRON,
EKTAFOS, SD 3562



Dimethyl phosphate ester of 3-hydroxy-
N,N-dimethyl-cis-crotonamide

The photodegradability of dicrotophos (Bidrin, Shell Chemical Co., purity and formulation unspecified) was studied by exposing dicrotophos (amount uncertain) to a sunlamp (quality and intensity of emitted light unspecified) at an unspecified temperature. Dicrotophos was also exposed to an elevated temperature (38 C), presumably in the dark. Samples were chemically analyzed (no details or citations provided) after exposure for 1, 2, and 4 hours.

REPORTED RESULTS:

Upon exposure to 38 C for 1, 2, and 4 hours, 50, 40, and 14% of the initial dicrotophos, respectively, were recovered, indicating a rapid volatilization of the compound. No photodegradation occurred, however, since 86, 72, and 46% of the initial dicrotophos were recovered after exposure to the sunlamp for the same respective intervals.

DISCUSSION:

1. The methods were very poorly presented. The purity of the test compound and a description of the light source were not given. Data on the incubation conditions were incomplete, and information on the analytical methods was totally absent. It is even unclear whether the dicrotophos was in solution or on a surface.

2. An appropriate control was not included to help determine if dicrotophos losses from the sunlamp-exposed sample were due to volatilization rather than photolysis.

CASE GSC035 DICROTOPHOS STUDY 2 PP 12/03/80

CHEM 035201

BRANCH EFB DISC 30 TOPIC C5052010 GUIDELINE 40 CFR 163.62-8b/c

FORMULATION 04 - GRANULAR

FICHE/MASTER ID 00013470 CONTENT CAT 01

Osgerby, J.M.; Clarke, D. (1965) Project Progress Report PPR FD/5/65: The Stability of Bidrin in Soil: Project F 18. Includes method dated Feb 1, 1965. (Unpublished study received Jan 28, 1966 under 201-142; prepared by Shell Research, Ltd., submitted by Shell Chemical Co., Washington, D.C.; CDL:000834-AF)

FICHE/MASTER ID: 00028571

CITATION: Osgerby, J.M.; Woodburn, A.T. 1965. Project Progress Report PPR FD 48/65: The adsorption and decomposition of Bidrin and Azodrin in soil: Project F 18. (Unpublished report prepared by Shell Research Ltd.)

SUBST. CLASS = S.

DIRECT EVE TIME = 12 (MH) START-DATE END DATE

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CONCLUSIONS:

Microbiological - Effects of Microbes on Pesticides

1. This portion of the study is scientifically valid.

2. In an in vitro, soil-inoculated system, virtually all (95%) of the initial dicrotophos is lost within 12 days. In this system, microbial metabolism is the major route of loss although volatilization may also be contributory.

Metabolism - Aerobic Soil

1. This portion of the study is scientifically valid.

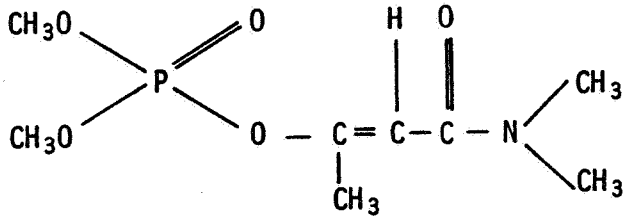
2. Dicrotophos degradation is rapid in most soils and is largely due to microbial metabolism. The half-life is usually 3-15 days. Degradation of technical dicrotophos is about twice as rapid as that of granular formulations.

Mobility - Leaching

This portion of the study is scientifically invalid because the analytical method for determining dicrotophos was not presented and controls were not run.

MATERIALS AND METHODS:

DICROTOPHOS, BIDRIN, C 709, CARBICRON, EKTAFOS, SD 3562



Dimethyl phosphate ester of 3-hydroxy-N,N-dimethyl-cis-crotonamide

Microbiological

A nutrient salt solution containing dicrotophos (Bidrin, Shell Chemical Co., purity and formulation unspecified) at 50 ppm was inoculated with about 2% (w:w) soil A (Table 1) and incubated at 22 C for 30 days. After various time intervals, centrifuged aliquots were analyzed spectrophotometrically (240 nm) and the dicrotophos concentration was determined from a standard curve after a soil blank correction was applied. Sodium azide-treated (0.01%) samples (intended as sterile controls) were also treated with dicrotophos.

Soil Metabolism

Soils A, 1, 2, and W1 (Table 1) were sieved to <2 mm, air dried (except soil A), and treated with either technical dicrotophos (Bidrin, 90% ai, Shell Chemical Co.) or one of two granular dicrotophos formulations (Bidrin, 5% ai, Shell Chemical Co.) at 2,000 ppm. Soil 1 had been stored in an air-dried condition for at least 3 weeks before use. Autoclaved soils were also treated with granular dicrotophos and served as sterile controls. Duplicate soil samples were incubated in screw-capped glass bottles in the dark at 22 C (moisture content unspecified).

Samples were periodically collected, ground with anhydrous Na_2SO_4, and extracted with chloroform. The chloroform extracts were evaporated almost to dryness and dissolved in carbon tetrachloride. The recovery of dicrotophos was between 90 and 95%. Infrared spectra were obtained, and the intensities of the peaks at 930 and 1,125 cm^{-1} were used to quantitate the dicrotophos concentrations upon comparison with a standard curve.

Leaching

The soils (Table 1) were sieved to <2 mm and air dried. An aqueous solution (concentration unspecified) of dicrotophos (Bidrin, Shell Chemical Co., formulation and purity not specified) was shaken with a known mass of soil until equilibrium was obtained (method of determining equilibrium unspecified). The dicrotophos concentration in the solution was measured to determine the amount adsorbed. The soil solution was then diluted with water, equilibrated for 2 hours (unspecified whether suspension was agitated or stationary), and analyzed for dicrotophos. This desorption process was repeated several times.

REPORTED RESULTS:

Microbiological

Approximately 52, 68, and 95% of the initial dicrotophos was lost from the soil-inoculated salts solution after incubation for 4, 6, and 11-12 days, respectively. In the sodium azide-treated suspensions, only 15, 30, and 25% of the initial dicrotophos was lost after the respective intervals.

Soil Metabolism

In soil A, technical dicrotophos was degraded with a half-life of 3 days, and the granular formulations had half-lives of 5-7 days. Technical dicrotophos had half-lives of 3 and 15 days in soils 2 and W1, respectively. The comparatively slow degradation in soil W1 was suspected as being due to adsorption of dicrotophos by the large amounts of organic matter present (Table 1). The half-life of a granular formulation was >60 days in soil 1, probably due to low microbial numbers caused by lengthy storage of the soil in an air-dried condition. No decomposition of granular dicrotophos occurred in sterile soil A after incubation for 31 days. Dicrotophos degradation in soil follows first-order kinetics, which suggests that soil organisms continuously synthesize the enzymes required for metabolism of this compound.

Leaching

The Freundlich adsorption coefficients (K) were 1.91, 0.99 and 0.95, and 0.35, for the clay, sandy clay loams, and sandy loam soils, respectively. The 1/n values were less than unity for the clay and sandy clay loam soils and greater than unity for the sandy loam soil. The $Q \left(\frac{K \cdot 100}{\% \text{ organic matter}}\right)$ values were between 11.5 and 17.6 for all of the soils (Table 2).

The desorption of dicrotophos from soil was not wholly reversible, because each soil showed hysteresis. This indicated that desorption was a slow process.

DISCUSSION:

1. The sterility of the sodium azide-treated controls was not determined, although it is quite likely that sterilization occurred. The dicrotophos losses could thus be due to microbial metabolism or volatilization, or both.

2. A very high dicrotophos concentration (2,000 ppm) was used for the soil metabolism study. This high dosage had no apparent effect on dicrotophos metabolism, since first-order kinetics were followed and the rate was rapid.

3. The half-life of a granular formulation of dicrotophos in soil 1 was over 60 days. This value is much higher than that for the technical or granular formulations in other soils (3-15 days). Since the soil was treated differently in this case (stored air dried for over 3 weeks), the data obtained are atypical and unreliable.

4. The analytical method used to determine the concentration of dicrotophos in the soil suspension was not presented. Recovery data and method sensitivity also were not presented. There is no indication that controls were run.

5. The experimental procedures for the leaching portion of the study were not described in sufficient detail to determine their validity. The concentration of dicrotophos solution applied and the amount of soil used were not reported. The amount of water added during each step of the desorption procedure was not reported.

6. The desorption of dicrotophos reportedly was a slow process. However, data showing the amount of dicrotophos desorbed over time were not presented to support that conclusion.

Table 1. Soil characteristics.

Soil	Texture	Organic matter (%)	Sand (%)	Silt (%)	Clay (%)	pH	Field moisture capacity (%)
A	Sandy clay loam	7.1	58.1	16.8	25.1	7.6	--
1	Sandy loam	2.0	80.5	8.8	10.7	6.8	15
2	Sandy clay loam	6.8	66.5	11.3	22.1	7.5	35
NC	Sandy clay loam	5.4	49.1	13.9	37.0	7.5	27
W1	Clay	16.5	14.1	8.9	77.0	4.7	38

Table 2. Adsorption constants for dicrotophos

Soil	Texture	K	$\frac{1}{n}$	Q
W1	Clay	1.91	0.62	11.5
2	Sandy clay loam	0.99	0.89	16.0
NC	Sandy clay loam	0.95	0.97	17.6
1	Sandy loam	0.35	1.15	17.6

CASE 050035 DICROTOPHOS STUDY 3 PM 12/03/80

CHEM 035201

BRANCH EFB DISC 30 TOPIC 0505

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID 05015927 CONTENT CAT 01

Pandey, S.Y.; Agnihotri, N.P. (1975) Effect of fertilisation on the degradation of dicrotophos, disulfoton and phorate in soil. Fertiliser News 20(11):32-33.

SUBST. CLASS = S.

DIRECT RVW TIME = 6 (MH) START-DATE END DATE

REVIEWED BY: W. Hazel
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SIGNATURE: DATE:

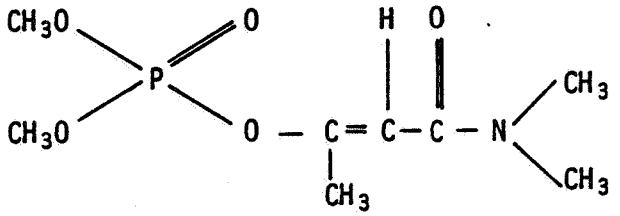
CONCLUSION:

Metabolism - Aerobic Soil

This study is scientifically invalid because no controls were included and because the aerobic or anaerobic condition of the soil is unknown.

MATERIALS AND METHODS:

DICROTOPHOS, BIDRIN, C 709, CARBICRON,
EKTAFOS, SD 3562



Dimethyl phosphate ester of 3-hydroxy-
N,N-dimethyl-cis-crotonamide

Dicrotophos (5% ai granular, source unspecified), at 5 ppm, was either mixed with or banded onto duplicate (50 g) samples of a sandy loam soil (0.32% C, 73.2% sand, 7.8% silt, 19.8% clay, pH 8.0, and CEC 2.1 meq/100 g). Identically treated samples were also fertilized with the equivalent of 110, 30, and 15 kg/ha of nitrogen, phosphorus, and potassium, respectively. All samples were moistened to field capacity and incubated at 30 C for 75 days (lighting conditions unspecified). After various intervals, samples were air dried and 25 g soil was mixed with NH_3 solution (solvent, concentration, and purpose unspecified), activated charcoal, and florisil. The mixture was placed in a column containing Na_2SO_4 and eluted with acetone. The eluate was analyzed for dicrotophos by a cited colorimetric method (Jain et al. 1974. Indian J. Plant Protect. 1:37-42).

REPORTED RESULTS:

No detectable dicrotophos remained in the soil, regardless of treatment, after incubation for 75 days (Table 1). The half-life of dicrotophos for all treatments was between 15 and 30 days. The different application methods (mixing or banding) and the exclusion or inclusion of fertilizer had little effect on the rate of dicrotophos disappearance.

DISCUSSION:

1. It is unknown whether the soils were incubated in sealed or open containers. Since the soils were saturated with water at the beginning of the incubation period, anaerobic conditions could develop if the containers were sealed. The soils could have dried out if the containers were open, since no mention was made of adding water during the 75-day incubation period.

2. No controls were included. No provision was made to determine if the dicrotophos losses were due to volatilization.

3. The dicrotophos levels in soil were not determined immediately after application. The levels were assumed to be identical with the amounts theoretically applied. No recovery data were presented for the method, although such information could be given in the cited reference.

4. Duplicate 50-g soil samples were incubated for each treatment (100 g total). However, seven 25-g subsamples (175 g total) were analyzed for each treatment. This discrepancy may be the result of a typographical or a literary error.

Table 1. Dicrotophos losses from a sandy loam soil treated with dicrotophos at 5 ppm.

Days of incubation	Dicrotophos concentration (percent of applied)			
	Unfertilized		Fertilized	
	Dicrotophos mixed with soil	Dicrotophos banded on soil	Dicrotophos mixed with soil	Dicrotophos banded on soil
0	100	100	100	100
3	82	87	84	88
7	64	76	68	75
15	54	62	58	60
30	30	40	36	42
45	18	20	16	22
60	5	8	3	10
75	0	0	0	0

CASE GS0035 DICROTOPHOS STUDY 4 PP 12/03/80

CHEM 035201

BRANCH EFB DISC 20 TOPIC 150520

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID C0013471 CONTENT CAT 02

Bull, D.L.; Lindquist, D.A. (19??) Rate of Absorption of Bidrin into Plant Parts. (Unpublished study received Jan 28, 1966 under 201-142; prepared by U.S. Agricultural Research Service, Entomology Research Div., Cotton Insects Research Branch, submitted by Shell Chemical Co., Washington, D.C.; CDL:000834-AN)

SUBST. CLASS = S.

DIRECT RVW TIME = 8½ (MH) START-DATE END DATE

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CONCLUSIONS:

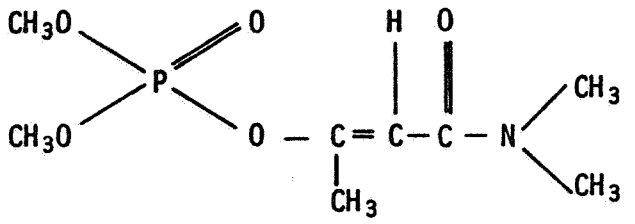
Reentry

1. This study is scientifically valid.

2. In a greenhouse study, dislodgeable radioactivity on leaves and cotyledons of cotton treated with [^{32}P]dicrotophos decreased to 16-31% of the applied radioactivity within 24 hours after treatment.

MATERIALS AND METHODS:

DICROTOPHOS, BIDRIN, C 709, CARBICRON, EKTAFOS, SD 3562



Dimethyl phosphate ester of 3-hydroxy-N,N-dimethyl-cis-crotonamide

[^{32}P]Dicrotophos (Bidrin, Shell Chemical Co., purity unspecified) was uniformly applied (20 µg in water) to the leaf surfaces of cotton (presumably only one surface per leaf). The plants were maintained in a greenhouse under normal lighting conditions or in darkness. Leaves were harvested at various time intervals, and the upper or lower leaf surfaces were washed with water to determine dislodgeable residue levels. Then the leaf was extracted with an acetone:water solution (ratio unspecified) to quantify intrafoliar residues. The washings and extracts were radioassayed. A similar study was conducted by applying 20 µg of [^{32}P]dicrotophos to the cotyledons of cotton seedlings.

REPORTED RESULTS:

Dislodgeable (water wash) and extractable radioactivity data are presented in Table 1. Radioactivity in the acetone:water extracts increased rapidly during the first 8 hours and then leveled off. Radioactivity in the water washings decreased rapidly during the first 8 hours and then decreased slowly thereafter. Volatilization reportedly accounted for 25-32% of the lost radioactivity within the first 24 hours.

DISCUSSION:

1. The samples were radioassayed. Therefore, it is not known whether the recovered radioactivity was present in dicrotophos or its degradation products.

2. Method sensitivity and recovery levels were not reported.

3. The losses attributed to volatilization were determined by taking the difference between the applied and recovered radioactivity values. Because no volatile products were trapped, the radioactivity unaccounted for cannot be definitively attributed to volatilization. Since dicrotophos is a systemic insecticide, some of these losses may be due to translocation to other parts of the plant.

Table 1. Absorption of topically applied [^{32}P]dicrotophos by upper and lower surfaces of cotton leaves, and upper surfaces of cotton cotyledons.[a]

Sample and lighting conditions	Hours after treatment	Upper surface			Lower surface		
		Water dislodgeable	Acetone:water extractable	Volatile losses	Water dislodgeable	Acetone:water extractable	Volatile losses
Cotton leaf (light)	1	74	14	12	67	19	14
	2	56	29	15	54	29	17
	4	40	41	19	40	41	19
	8	36	44	20	16	50	34
	24	31	44	25	18	56	26
Cotton leaf (darkness)	2	68	11	21	--[b]	--	--
	4	57	22	21	--	--	--
	8	42	34	24	--	--	--
	24	21	47	32	--	--	--
Cotton cotyledon (unspecified)	1	67	27	6	--	--	--
	2	37	47	16	--	--	--
	4	34	43	23	--	--	--
	8	17	55	28	--	--	--
	24	16	57	28	--	--	--
	48	10	57	33	--	--	--
	72	15	59	26	--	--	--

[a]Percent of applied radioactivity.

[b]Data were not reported.

STUDY 5

CHEMICAL: DICROTOPHOS

FORMULATION: 04 - Granular

FICHE/MASTER ID: 00013512

CITATION: Elgar, K.E., and I.A. MacDonald. 1966. Analysis of crops for residues of Bidrin and its metabolites. J. Sci. Food Agric. 17:500-505.

DIRECT RVW TIME = 9 (MH) START-DATE END DATE

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CONCLUSIONS:

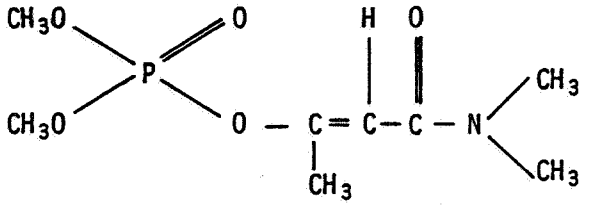
Field Dissipation - Terrestrial

1. This study is scientifically valid.

2. Dicrotophos dissipates rapidly in clay loam soil. The half-life of dicrotophos was less than 1 week and dicrotophos was not detected 8 weeks after treatment at 2, 4, or 8 lb/A.

MATERIALS AND METHODS:

DICROTOPHOS, BIDRIN, C 709, CARBICRON,
EKTAFOS, SD 3562



Dimethyl phosphate ester of 3-hydroxy-
N,N-dimethyl-cis-crotonamide

Clay loam field plots (soil characteristics not given) in the United Kingdom were treated with dicrotophos (Bidrin, 5% granular, Shell Research Ltd.) at 2, 4, or 8 lb/A. Soil samples were collected to an unspecified depth at unspecified intervals after treatment. The intervals between treatment and receipt of samples for analysis were 0, 1, 2, 4, and 8 weeks. The samples were stored at -20 C until analysis.

Duplicate subsamples were blended with chloroform and filtered. The filtrate was dried with anhydrous Na_2SO_4 and stored in the dark. The filtrate solvent was changed from chloroform to hexane by the repeated evaporation of solvent to a small volume followed by the addition of hexane. Dicrotophos residues were transferred from hexane to water by partitioning. The recovery of dicrotophos from soil was 81%.

An aliquot of the aqueous extract was incubated with a solution containing human blood plasma, Giang and Hall buffer (Giang and Hall. 1951. Anal. Chem. 23:1830), and distilled water for 30 minutes at 25 C. Aqueous acetylcholine chloride was added to the mixture and incubated for 60 minutes. The pH of each soil extract reaction mix was measured with a pH meter after each incubation period. The dicrotophos present was determined in micrograms from a calibration curve prepared with solutions containing known amounts of dicrotophos. The limit of detection was 0.05 ppm.

Samples from the plot treated at 8 lb/A were analyzed for the metabolite mono-N-methylcrotonamide by the following method. The extract solvent was changed from chloroform to carbon tetrachloride and evaporated to a small volume. The residue was dissolved in chloroform:carbon tetrachloride (5:95, v:v). Mono-N-methylcrotonamide was separated from dicrotophos by column chromatography. Dicrotophos was eluted from the column with carbon tetrachloride and then mono-N-methylcrotonamide was eluted with benzene or methylene chloride. Each eluate solvent was changed to hexane and then partitioned with water. The water extracts were analyzed by the acetylcholinesterase method described above. The efficiencies for the extraction procedure were 90-100% for dicrotophos and 65-80% for mono-N-methylcrotonamide. The limit of detection for mono-N-methylcrotonamide was 0.01 ppm.

REPORTED RESULTS:

Dicrotophos levels in clay loam soil treated at 2, 4, or 8 lb/A declined from 2.4-11.3 ppm at week zero to <0.05 ppm at 8 weeks between treatment and sample receipt (Table 1). Samples from the plot treated with dicrotophos at 8 lb/A did not contain mono-N-methylcrotonamide at detectable levels.

DISCUSSION:

1. The method used to determine dicrotophos levels in soil was not specific for dicrotophos but determined the levels of all acetylcholinesterase inhibitors present in the soil. The levels of acetylcholinesterase inhibitors that may have been present in the soil prior to treatment with dicrotophos cannot be determined because (1) pretreatment samples were not collected, (2) a control plot was not run, and (3) a history of pesticide application to the plots was not provided. However, since acetylcholinesterase inhibitor levels declined below the detection limit of the method, the lack of this information does not affect the scientific validity of the study.

2. Important experimental parameters such as sampling depths, climatic data, and the number of samples collected were not presented.

3. The actual treatment-to-sampling intervals were not given. Rather, since samples were shipped from the treated field to the site of analysis, intervals from treatment to sample receipt were given. Since the treated field and the analytical laboratory were both located in the United Kingdom, however, it is assumed that the transit time was brief.

Table 1. Dicrotophos dissipation in a clay loam soil.

Application rate (lb/A)	Dicrotophos levels (ppm) in soil after various intervals of treatment to sample receipt				
	0 week	1 week	2 weeks	4 weeks	8 weeks
2	2.4	0.9	0.5	0.4	<0.05
4	5.6	1.7	1.1	1.3	<0.05
8	11.3	4.7	2.9	3.7	<0.05

STUDY 6

CHEMICAL: DICROTOPHOS

FORMULATION: 01 - Technical Chemical

FICHE/MASTER ID: 05013057

CITATION: Brown, N.P.H. 1966. Stability of agricultural chemicals. I. Hydrolytic and thermal stabilities of phosphorylated crotonamides. J. Sci. Food Agric. 17:510-517.

DIRECT RVW TIME = 8 (MH) START-DATE END DATE

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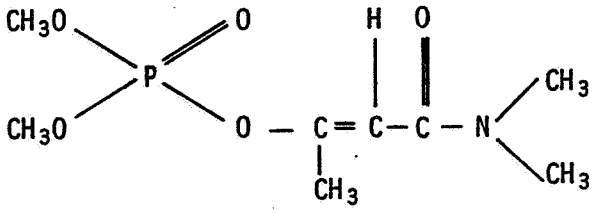
CONCLUSION:

Degradation - Hydrolysis

This study is scientifically invalid because the dicrotophos solutions were not maintained in the dark.

MATERIALS AND METHODS:

DICROTOPHOS, BIDRIN, C 709, CARBICRON, EKTAFOS, SD 3562



Dimethyl phosphate ester of 3-hydroxy-N,N-dimethyl-cis-crotonamide

The hydrolysis rates of dicrotophos at various concentrations (Table 1) were studied at pH 2.5 (in distilled water), pH 7 (in phosphate buffer), and pH 12 (in 0.1 N NaOH) and at various temperatures. Samples were taken from solutions at pH 2.5 and 12 after various time intervals (not specified) and examined by acid-base potentiometric titration to quantify the rate of formation of acids and bases resulting from hydrolysis and thus to determine hydrolysis rates. Samples obtained from the phosphate buffer solution (pH 7) were extracted with chloroform. The extract was dried in a water bath, and the residue was redissolved in carbon tetrachloride. The dicrotophos concentration was determined by IR spectroscopy.

To obtain adequate quantities of hydrolysis products for identification, 10% (w:w) solutions of dicrotophos (Bidrin, technical; 92% cis, 6% trans; Shell Chemical Co.) in distilled water (pH 2.5) or in 2 N NaOH were refluxed for 6 hours under unspecified conditions. The reaction products were fractionated by distillation and the fractions obtained were then analyzed by IR spectroscopy, paper chromatography, and potentiometric titration.

REPORTED RESULTS:

After 6 hours of refluxing, dicrotophos in alkaline solution was degraded to form a dimethyl phosphate and a crotonamide moiety (Figure 1). The crotonamide group was further decomposed to produce CO_2, acetone, and dimethylamine. The dimethyl phosphate ion was not further hydrolyzed. Under acidic conditions, dicrotophos degradation proceeded by initial loss of a methoxy group from the phosphate ester followed by the rapid breakdown of the crotonamide group (Figure 1). The course of the acid hydrolysis was further confirmed by potentiometric titration of the hydrolysis mixtures. Identified degradation products were methanol, acetone, orthophosphoric acid, methyl phosphoric acid, N,N-dimethyl-acetoacetamide, and CO_2. The rate constants for dicrotophos hydrolysis under various pH and temperature conditions are given in Table 1. At 50 C, the hydrolysis rate increased slightly as the pH was increased up to 7, but then it increased rapidly with increasing pH values.

DISCUSSION:

1. The solutions were not kept in darkness. Therefore this study is considered invalid.

2. The hydrolysis studies were largely conducted under extreme conditions (pH and temperature). Thus the data cannot be applied to natural environmental conditions.

3. The hydrolysis products identified from refluxed dicrotophos solutions are not necessarily the same as those unidentified products formed under the controlled conditions of hydrolysis.

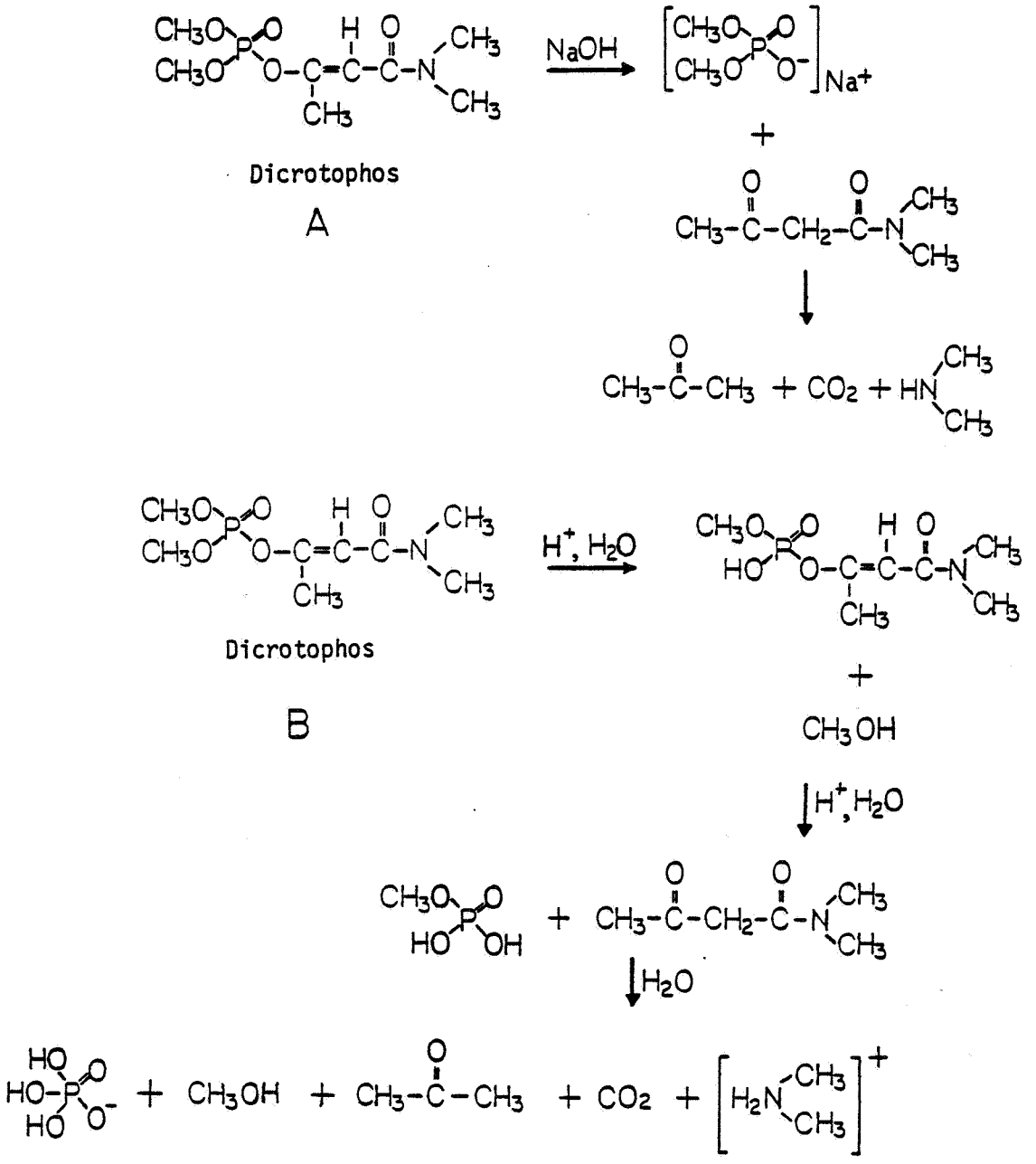


Figure 1. Proposed hydrolysis pathways under alkaline (A) and acidic (B) conditions based on products obtained by refluxing at pH 12 and 2.5, respectively.

From Brown (05013057).

Table 1. Hydrolysis rate constants for dicrotophos.

Temperature (C)	Concentration (mmol/l)	pH	Rate constant	
			1st order (sec^{-1})	2nd order $(mol/l)^{-1} sec^{-1}$
100	38	2.5	2.3×10^{-4}	--
100	380	2.5	1.0×10^{-4}	--
100	38	7.0	2.1×10^{-4}	--
100	137	7.0	2.1×10^{-4}	--
50	38	2.5	1.2×10^{-6}	--
50	38	7.0	2.5×10^{-6}	--
50	77	12.0	--	0.8×10^{-1}
50	87	12.0	--	1.3×10^{-1}
50	53	12.0	--	1.3×10^{-2}

STUDY 7

CHEMICAL: DICROTOPHOS

FORMULATION: 00 - Active Ingredient

FICHE/MASTER ID: 05012474

CITATION: Corey, R.A. 1965. Laboratory tests with Bidrin insecticide. J. Econ. Entomol. 58(1):112-114.

DIRECT RVW TIME = 7 (MH) START-DATE END DATE

REVIEWED BY: W. Hazel
TITLE: Staff Scientist
ORG: Enviro Control, Inc., Rockville, MD
LOC/TEL: 468-2500

SIGNATURE: W. Hazel DATE: Sept. 29, 1981

APPROVED BY:
TITLE:
ORG:
LOC/TEL:

SIGNATURE: DATE:

CONCLUSIONS:

Metabolism - Aerobic Soil

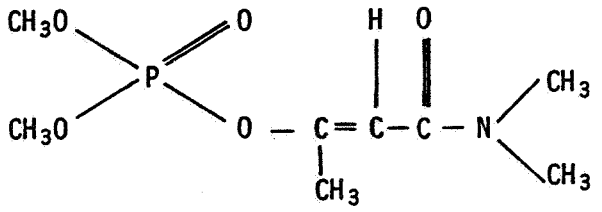
This portion of the study is scientifically invalid because incubation conditions were not described, analytical procedures were not given, and controls were not included.

Mobility - Leaching

This portion of the study is scientifically invalid because the bioassay procedures were not described.

MATERIALS AND METHODS:

DICROTOPHOS, BIDRIN, C 709, CARBICRON, EKTAFOS, SD 3562



Dimethyl phosphate ester of 3-hydroxy-N,N-dimethyl-cis-crotonamide

Soil Metabolism

[^{14}C]Dicrotophos (Bidrin, granular formulation; purity and source unspecified) was mixed with a sandy loam soil (not described). Air-dried soil and soils moistened to 50, 75, and 100% of field capacity were treated at 10 ppm. After incubation of duplicate samples for 7 or 8 days (temperature and lighting conditions unspecified), the soils were analyzed for [^{14}C]dicrotophos by liquid-liquid partition or paper chromatography (procedures not given).

Leaching

Dicrotophos (Bidrin; purity and source unspecified) was applied at 6 mg/5-inch pot to the surface of soil potting mix (not described) in which cotton seedlings were growing. The soil samples were leached with 25,100, or 400 ml of water. The leachates (0, 75, and 350 ml, respectively) were bioassayed for dicrotophos (method not given).

REPORTED RESULTS:

Soil Metabolism

After incubation for 7 or 8 days, 80.5, 18.5, 8.8, and 6.8% of the applied [^{14}C]dicrotophos was recovered from air-dried soil, and from soil moistened to 50, 75, or 100% of field capacity, respectively. Data are means of two tests, one after 7 days and one after 8 days of incubation.

Leaching

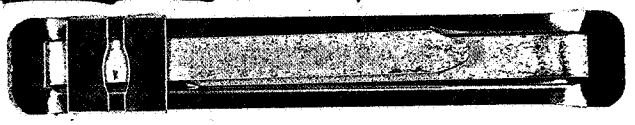
The leachates from pots leached with 100 and 400 ml of water contained 20 and 75% of the applied dicrotophos, respectively.

DISCUSSION:

1. No untreated control soils were included.

2. Neither the analytical methods for the soil metabolism portion nor the procedures for bioassay of dicrotophos in the leaching portion of the study were given. It is thus impossible to determine whether dicrotophos or its degradates were being measured and, in the case of the soil metabolism portion, whether total ^{14}C or solely [^{14}C]-dicrotophos was being quantified.

3. Incubation conditions were unspecified for the soil metabolism portion of the study.



Azodrin (R)

$(CH_3O)_2P(O)OC(CH_3)=CHC(O)N(H)CH_3$

III ↑

$(CH_3O)_2P(O)OC(CH_3)=CHC(O)N(CH_2OH)CH_3$

II ↑

$(CH_3O)_2P(O)OC(CH_3)=CHC(O)N(CH_3)CH_3$

BIDRIN

I ↓

$(CH_3O)(HO)P(O)OC(CH_3)=CHC(O)N(CH_3)CH_3$

V

Sugar conjugate of II

VIII

(not found in animals) ↓

$(CH_3O)_2P(O)OH$

IV ↑

$(CH_3O)_2P(O)OC(CH_3)=CHC(O)OH$

VI ↓

$(CH_3O)(HO)P(O)OC(CH_3)=CHC(O)OH$

VII ↓

$(CH_3O)(HC)P(O)OH$

IX ↓

H_3PO_4

Proposed Pathway for the Degradation of BIDRIN

in Plants and Animals