DYNAMAC
CORPORATION

DIALLATE

Task 1: Review and Evaluation of Individual Studies

Contract No. 68-01-6072

Final Report

October 29, 1982

Submitted to:

Environmental Protection Agency
Arlington, Virginia 22202

Submitted by:
Dynamac Corporation
Enviro Control Division
The Dynamac Building
11140 Rockville Pike
Rockville, MD 20852

DIALLATE

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CASE GS 0098 DIALLATE STUDY 1 PM 04/12/82

CHEM 078801 Diallate

BRANCH EFB DISC 30 TOPIC 050525 GUIDELINE 40 CFR 163.62-9b/c/d

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID 00068698 CONTENT CAT 01

Smith, A.E., and A. Fitzpatrick. 1970. The loss of five thiolcarbamate herbicides in nonsterile soils and their stability in acidic and basic solutions. J. Agric. Food Chem. 18(4):720-722. Also In unpublished submission received June 23, 1977 under 476-2182; submitted by Stauffer Chemical Co., Richmond, CA; CDL:230714-D.

SUBST. CLASS = S. OTHER SUBJECT DESCRIPTORS SEC: EFB -30-05052005

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

REVIEWED BY: W. Spangler and T. Opeka
TITLE: Staff Scientists
ORG: Dynamac Corp., Enviro Control Division, Rockville, MD
LOC/TEL: 468-2500

SIGNATURE: W. Spangler Timothy J. Opeka DATE: Sept. 17, 1982

APPROVED BY:
TITLE:
ORG:
LOC/TEL:

SIGNATURE: DATE:

CONCLUSIONS:

Degradation - Hydrolysis

This portion of the study is scientifically invalid because dark controls were not included to differentiate between hydrolysis and photolytic degradation.

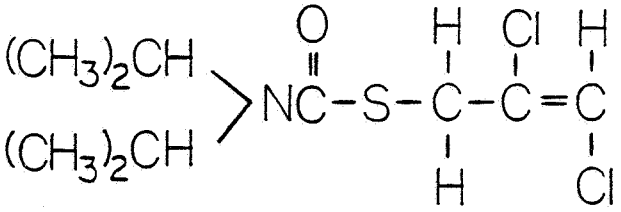
Metabolism - Aerobic Soil

1. This portion of the study is scientifically valid.

2. Diallate degraded fairly rapidly with a half-life of 4 weeks in Weyburn loam and 5-6 weeks in Regina clay. The soils were incubated in the dark at 25 C and moisture at field capacity.

MATERIALS AND METHODS:

DIALLATE, AVADEX, DATC, CP 15336



S-(2,3-dichloroallyl)-diisopropylthiocarbamate

Degradation - Hydrolysis

Diallate (analytical grade, Monsanto Chemical Co.) was hydrolyzed using 4-36 N sulfuric acid in step intervals of two normality units. Ten milliliters of each acid solution was added to 10 ml of 8.5 ppm diallate solution in 50 ml glass stoppered tubes. The tubes were treated in an oil bath at 95 ± 2 C or 75 ± 2 C for 1 hour, cooled, diluted with 50 ml cold distilled water, and extracted with 20 ml of benzene. The organic phase was dried over anhydrous sodium carbonate and analyzed for diallate by using the electron-capture GC method described by Smith (J. Agric. Food Chem. 17:1052, 1969; Weed Res. 9:306, 1969).

Alkaline hydrolysis was carried out similarly with 8.5 ppm diallate solutions being treated with 2, 4, 6, 8, or 10 N sodium hydroxide to yield 1, 2, 3, 4, and 5 N solutions which were heated for 1 hour in an oil bath at 95 ± 2 C or 50 ± 2 C. After cooling, dilution, and benzene extraction, diallate was determined by using the GC method of Smith.

Metabolism - Aerobic Soil

Analytical grade diallate was added at 5 ppm to Regina clay and Weyburn loam soils (Table 1). Due to the limited aqueous solubility of diallate, it was applied to 2 kg batches of soil in hexane and 20 g aliquots of this were moistened to field capacity and placed into 70 ml screw cap bottles. Bottles were capped and incubated in the dark at 25 ± 2 C. A sample was removed for analysis after 24 hours of equilibration and at 2 week intervals thereafter for an unspecified period of time. Samples were solvent extracted and analyzed by the GC method described by Smith.

REPORTED RESULTS:

Degradation - Hydrolysis

Sulfuric acid at ∿11 N was required for 50% hydrolysis at 95 C for 1 hour and ∿13 N sulfuric acid was required for equivalent hydrolysis at 75 C for 1 hour. An additional peak was observed on GC chromatograms during acid hydrolysis.

Diallate was completely hydrolyzed in 1 N sodium hydroxide at 95 C for 1 hour and in 3 N sodium hydroxide at 50 C for 1 hour.

Metabolism - Aerobic Soil

Diallate degraded fairly rapidly in soils with a half-life of 4 weeks in Weyburn loam and 5-6 weeks in Regina heavy clay. Recovery of diallate from both soils, after a 24 hour equilibration period was >90%.

DISCUSSION:

1. In the hydrolysis experiment, dark controls were not included to differentiate between hydrolytic and photolytic degradation. In addition, the design was inadequate to determine half-lives and material balance, to identify hydrolytic products or to follow patterns of formation and decline of degradates.

2. In the metabolism experiment, the procedures and protocols were briefly described and referenced. A material balance was not performed and degradation products were not identified. It was not stated whether untreated control samples were included in the test.

Table 1. Soil characteristics.

Soil	Mechanical analysis (%)			Organic matter (%)	pH	Field capacity (% moisture)
	Sand	Silt	Clay			
Regina clay	3.5	22.5	74.0	4.0	7.5	40
Weyburn loam	45.0	37.0	18.0	6.5	7.0	28

1 1/2

5-6 wks

4 wks

CASE GS0098 DIALLATE STUDY 2 PM 04/12/82

CHEM 078801 Diallate

BRANCH EFB DISC --

FORMULATION 12 - EMULSIFIABLE CONCENTRATE

FICHE/MASTER ID No MRID CONTENT CAT --

Nassar, A.R., and W. Ebing. 1978. Photodecomposition and volatility of cis and trans diallate. Egyptian J. Soil Sci. 18(2):137-149.

SUBST. CLASS = S.

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

REVIEWED BY: W. Spangler
TITLE: Staff Scientist
ORG: Dynamac Corp., Enviro Control Division, Rockville, MD
LOC/TEL: 468-2500

SIGNATURE: W. Spangler DATE: Sept. 21, 1982

APPROVED BY:
TITLE:
ORG:
LOC/TEL:

SIGNATURE: DATE:

CONCLUSIONS:

Mobility - Laboratory Volatility

This portion of the study is scientifically invalid because analysis of volatile products was not performed to distinguish between volatilization of parent compound as opposed to formation of volatile degradation products. A materials balance was not conducted.

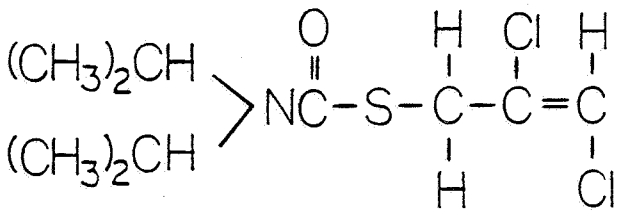
Degradation - Photodegradation on Soil

1. This portion of the study is scientifically valid.

2. Exposure of cis and trans diallate to artificial sunlight and to UV (peak emission at 254 nm), on soil and as thin films on glass, resulted in fairly rapid decomposition by photolysis. On soil, the half-lives of both cis and trans isomers were >8 days for exposure to UV irradiation compared to >16 days for artificial sunlight. The photodecomposition was accelerated in thin films, but was more pronounced under UV irradiation (half-lives were ∿3 days for both isomers) than under artificial sunlight (half-lives were ∿12 for cis and ∿8 for trans isomers). A major unidentified degradate appeared during exposure to UV and artificial sunlight, but was more pronounced in thin films exposed to UV light.

MATERIALS AND METHODS:

DIALLATE, AVADEX, DATC, CP 15336



S-(2,3-dichloroallyl)-diisopropylthiocarbamate

Mobility - Laboratory Volatility

Samples of a silty sand soil (pH 6.7, 1.4% C, water holding capacity 33.6%) were passed through a 2 mm sieve, and treated with diallate (Avadex EC 3.3 lb/gal, Badische Amilin-und Sodafabrik, Ludwigshafen, Germany) in acetone to yield a soil concentration of 4 ppm. Ten-gram samples were placed in Petri dishes and incubated in the dark at 25- and 35 ± 1 C. Duplicate samples were taken at various intervals up to 32 days, water was added to maximum water holding capacity, and the samples were extracted and analyzed for cis and trans isomers by using a GLC procedure described by Nassar et al. (The Third Pest Control Conference, Oct. 1976. Univ. of Ain Shamo, Faculty of Agric., (A.R.E.).

Aqueous volatility was studied in 5 ml aliquots of 100 ppm diallate incubated in the dark at 25- and 35 ± 1 C. Duplicate samples were withdrawn at 0, 1, 2, 4, 8, and 16 days, volume loss was measured and extraction and GLC analysis were performed to determine residual cis and trans isomers.

Degradation - Photodegradation on Soil

Ten-gram samples of a silty sand soil, containing diallate at 4 ppm, were weighed into 10-cm Petri dishes and covered with a quartz plate. The plates were irradiated under a 15-W lamp with peak emission at 254 nm or under a 400-W sun lamp with an emission spectrum similar to natural sunlight. Duplicate samples were removed at various intervals for extraction and analysis by electron capture GLC. Dark controls (aluminum foil covered) were also taken at each sample interval to compensate for thermal losses. Thin films were also prepared by drying 1 ml aliquots of an acetone solution (1 mg/ml) onto 5 cm Petri dishes. The films were covered with quartz plates and samples were exposed to UV and simulated sunlight for intervals up to 16 days. Duplicate samples and dark controls were removed at each interval, washed with 1 ml hexane and analyzed by using GLC.

REPORTED RESULTS:

Degradation - Photodegradation on Soil

Both cis and trans diallate isomers degraded rather rapidly under UV and simulated sunlight, but more so under UV irradiation (Table 1). The most rapid photodegradation (90.7 and 92.9% in 8 days for cis and trans isomers, respectively) occurred in thin films under UV irradiation. Both cis and trans isomers showed slower photodegradation on soil [(≤37% degraded under UV (in 8 days) and simulated sunlight (in 16 days)] compared to thin films (half-life ∿3 days for both isomers). The major degradate (unknown structure and concentration) was observed to appear first most rapidly in thin films under UV irradiation, but also appeared in thin films under simulated sunlight and on soil irradiated with UV light. Although some unknown degradates appeared in dark controls extensive degradation of cis and trans diallate did not occur in 16 days. The major unknown degradate was not observed in controls.

Mobility - Laboratory Volatility

The evaporation of both isomers was lower from soil than from aqueous solutions (Table 2). While 52.7 and 58.6% of cis and trans diallate, respectively, remained in treated soil after 32 days at 25 C, (half-lives >32 days) only 18.1 and 39.8% remained in aqueous solution after 16 days at 25 C (half-lives ∿9 days for cis and ∿14 for trans). Diallate was presumed to codistill with water, but to evaporate more rapidly than water.

DISCUSSION:

Experimental procedures and protocols were generally acceptable with the exception of the laboratory volatility experiments. In the volatilization studies volatiles were not monitored to provide sufficient data to distinguish between the presumed volatilization of diallate and the formation of volatile degradation products. Also, degradates were not identified, and a materials balance was not conducted. It was unclear whether the soil samples were incubated at maximum water holding capacity or whether the aliquots removed for analysis were moistened to maximum water holding capacity prior to extraction and analysis.

Table 1. Photodegradation of cis and trans diallate.

Time	% Degradation							
	On soil				In thin-film			
	UV		Sunlamp		UV		Sunlamp	
	cis	trans	cis	trans	cis	trans	cis	trans
0	0	0	0	0	0	0	0	0
¼ hr	--[a]	--	--	--	9.3	9.0	--	--
½	--	--	--	--	10.3	10.8	--	--
1	--	--	--	--	11.9	13.6	--	--
2	--	--	--	--	13.9	15.1	--	--
4	--	--	--	--	14.9	16.3	--	--
8	--	--	--	--	16.5	20.5	--	--
16	--	--	--	--	22.2	26.5	--	--
1 day	17.0	13.0	15.6	9.2	23.7	29.5	6.8	10.0
2	22.0	20.9	18.7	14.3	31.2	40.1	17.8	20.7
4	27.5	27.5	20.4	19.1	57.6	70.1	24.0	36.2
8	37.0	37.0	23.7	23.5	90.7	92.9	41.2	55.4
16	--	--	36.0	32.9	--	--	61.0	63.9

[a]No data reported.

Table 2. Volatilization of cis and trans diallate.

	% Volatilization									
	On soil				In solution					
	25 C		35 C		25 C			35 C		
Time (days)	cis	trans	cis	trans	cis	trans	H_2O	cis	trans	H_2O
0	0	0	0	0	0	0	0	0	0	0
1	21.3	22.1	35.2	33.0	9.0	8.5	4.0	18.9	8.5	8.0
2	30.6	28.6	44.1	38.6	18.1	12.2	6.0	75.7	72.3	14.0
4	32.4	30.7	52.0	46.2	25.4	15.6	8.0	89.2	89.2	24.0
8	37.0	34.3	62.0	57.5	42.7	25.7	13.0	94.6	93.8	44.0
16	44.5	40.0	75.6	70.9	81.9	60.2	19.0	100	100	72.0
32	47.3	41.4	--[a]	--	--	--	--	--	--	--

[a]No data reported.

CASE GS 0098 DIALLATE STUDY 3 PM 04/12/82

CHEM 078801 Diallate

BRANCH EFB DISC 30 TOPIC 050525 GUIDELINE 40 CFR 163.62-9b/c/d

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID 00068700 CONTENT CAT 01

Koren, E., C.L. Foy, and F.M. Ashton. 1968. Phytotoxicity and persistence of four thiocarbamates in five soil types. Weed Sci. 16:172-175. Also In unpublished submission received June 23, 1977 under 476-2182; submitted by Stauffer Chemical Co., Richmond, CA.; CDL:230714-F.

SUBST. CLASS = S. OTHER SUBJECT DESCRIPTORS PRIM: EEB -20-2010

DIRECT RVW TIME = 4½ (MH) START-DATE END DATE

REVIEWED BY: W. Spangler
TITLE: Staff Scientist
ORG: Dynamac Corp., Enviro Control Division, Rockville, MD
LOC/TEL: 468-2500

SIGNATURE: W. Spangler DATE: Sept. 22, 1982

APPROVED BY:
TITLE:
ORG:
LOC/TEL:

SIGNATURE: DATE:

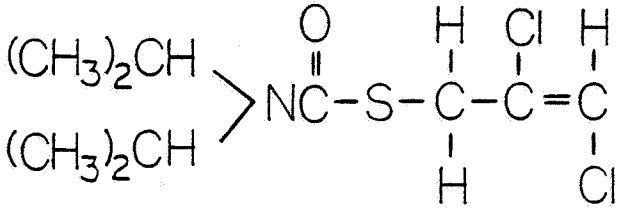
CONCLUSION:

Metabolism - Aerobic Soil

This study is scientifically invalid because experimental procedures and protocols were inadequate to provide direct support for presumed aerobic soil metabolism; only summary data were presented. Analyses were not performed for the parent compound or degradates, a half-life was not determined, and a materials balance was not conducted.

MATERIALS AND METHODS:

DIALLATE, AVADEX, DATC, CP 15336



S-(2,3-dichloroallyl)-diisopropylthiocarbamate

The phytotoxicity and persistence of diallate (formulation and source unspecified) was studied in five soil types (Table 1). Diallate was added at 0.1-102.4 ppm (by weight) to each soil by mixing aqueous solutions with 600 g of soil in metal cans, except for Staten Island peaty muck where only 300 g were used. Both non-sterile and steam sterilized samples of each soil were used. The soils were seeded with barnyard-grass and covered with 1 cm of treated soil. Sufficient soil moisture was maintained for growth, and plants were harvested after 26 days for size and weight determinations. To determine residual activity, the soils were dried for 17 days, pulverized, mixed, the previous harvest residue was added back, and soils were returned to their original cans for a second and third cycle of planting.

REPORTED RESULTS:

Sterilization of the soils resulted in higher persistence of diallate phytotoxicity (slower inactivation) than in non-sterile soils indicating metabolism to less toxic intermediates by soil microorganisms. The effect was greater in Stockton adobe sandy loam, clay loam, and Hesperia sandy loam than in peaty muck or sand.

DISCUSSION:

The data presented are not sufficient to provide direct support for aerobic soil metabolism; however, the study provided indirect evidence which indicates that diallate is metabolized by microorganisms in non-sterile soils.

Table 1. Soil characteristics.

Soil	Mechanical analysis (%)			Organic matter (%)	pH	Moisture equivalent % ($^1/_3$ atm)
	Sand	Silt	Clay			
Staten Island peaty muck	62.4	30.4	7.2	51.8	5.3	49.0
Stockton adobe sandy loam[a]	62.4	26.4	11.2	7.7	6.4	18.0
Yolo clay loam	33.2	38.8	28.8	3.3	7.5	15.0
Hesperia sandy loam	68.4	26.4	5.2	1.7	7.5	9.0
Washed sand	94.2	3.8	2.0	0.5	7.1	1.8

[a]Reported as a clay.

CASE GS0098 DIALLATE STUDY 4 PM 04/12/82

CHEM 077801 Diallate

BRANCH EFB DISC 30 TOPIC 100520

FORMULATION 90 - FORMULATION NOT IDENTIFIED

FICHE/MASTER ID 00086386 CONTENT CAT 06

Smith, A.E. 1967? The analysis and degradation of diallate in soils. Canada, Dept. Agric.; unpublished study; CDL:091613-E.

SUBST. CLASS = S. OTHER SUBJECT DESCRIPTORS SEC: EFB -30-050530

DIRECT RVW TIME = 4½ (MH) START-DATE END DATE

REVIEWED BY: W. Spangler
TITLE: Staff Scientist
ORG: Dynamac Corp., Enviro Control Division, Rockville, MD
LOC/TEL: 468-2500

SIGNATURE: W. Spangler DATE: Sept. 23, 1982

APPROVED BY:
TITLE:
ORG:
LOC/TEL:

SIGNATURE: DATE:

CONCLUSIONS:

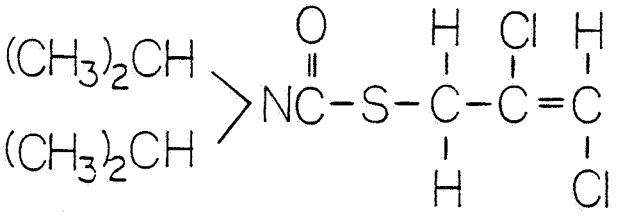
Metabolism - Aerobic Soil

1. This study is scientifically valid.

2. Diallate degraded with a half-life of <8 weeks in non-sterile Weyburn loam and Regina heavy clay soils incubated at 25 C and field capacity in the dark. Increasing soil moisture from permanent wilting point to field capacity enhanced diallate degradation. Soil sterilization greatly reduced the degradation rate (<10% of applied degraded in 4 weeks) indicating that microbial activity was primarily responsible for diallate losses.

MATERIALS AND METHODS:

DIALLATE, AVADEX, DATC, CP 15336



S-(2,3-dichloroallyl)-diisopropylthiocarbamate

Diallate (formulation and source unspecified) was added to 2-kg batches of sieved, air-dried Regina heavy clay (4% organic matter) and Weyburn loam (6.5% organic matter) soils in a 50-ml volume of hexane. After mixing, the resulting 4 ppm soil concentration was approximately two times the normal field application rate. The treated soils were added to 70-ml screw capped bottles as 20-g aliquots and brought to field capacity with distilled water (40% for Regina heavy clay and 30% for Weyburn loam). Sample sets were also prepared at permanent wilting point moisture levels (20% for clay and 12% for loam). Controls were prepared by sterilizing soil aliquots at 121 C for 8 hours and adding 35 µg diallate in 5-ml sterile distilled water. All bottles were incubated in the dark at 25 ± 1 C. Duplicate samples were removed after 0, 4, 6, and 8 weeks for extraction and analysis. Controls were analyzed after 4 weeks of incubation.

All samples were extracted by shaking with 75-ml of benzene:isopropanol (2:1, v:v) for 30 minutes. Isopropanol and acidic impurities were removed by shaking 25 ml of the extract with two 25 ml volumes of 3% aqueous sodium carbonate. The benzene layer was dried over anhydrous sodium carbonate, cleaned up by shaking with 0.2 g Nuchar Attaclay, and 5 µl aliquots were analyzed by GLC using an electron capture detector. Typical recovery of diallate from spiked clay and loam soil samples was 86-97%.

REPORTED RESULTS:

At field capacity moisture levels, 60% of the added diallate disappeared in 8 weeks from Regina heavy clay and 75% was lost from Weyburn loam. At the permanent wilting point moisture level, the respective rates of disappearance in 8 weeks were 20 and 45% from Regina heavy clay and Weyburn loam. Comparison to losses in sterile controls (<10% in 4 weeks) indicated that microbial degradation was responsible for losses under non-sterile, dark conditions, and that the microbial activity was favored at higher moisture levels.

DISCUSSION:

This study was generally well conducted, but the following data were not collected: major degradates were not identified or quantified; a material balance was not conducted; and diallate formulations were not given.

CASE GS 0098 DIALLATE STUDY 5 PM 04/12/82

CHEM 078801 Diallate

BRANCH EFB DISC --

FORMULATION 12 - EMULSIFIABLE CONCENTRATE

FICHE/MASTER ID No MRID CONTENT CAT --

Anderson, J.P.E., and K.H. Domsch. 1976. Microbial degradation of the thiolcarbamate herbicide, diallate, in soils and by pure cultures of soil microorganisms. Arch. Environ. Contam. Toxicol. 4:1-7.

SUBST. CLASS = S.

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

REVIEWED BY: W. Spangler
TITLE: Staff Scientist
ORG: Dyanamc Corp., Enviro Control Division, Rockville, MD
LOC/TEL: 468-2500

SIGNATURE: W. Spangler DATE: Sept. 23, 1982

APPROVED BY:
TITLE:
ORG:
LOC/TEL:

SIGNATURE: DATE:

CONCLUSIONS:

Metabolism - Aerobic Soil

1. This portion of the study is scientifically valid.

2. Diallate was degraded rapidly in non-sterile soils with half-lives of <4 weeks as opposed to >20 weeks in sterile soils. Similar results were obtained when [^{14}C]diallate added to non-sterile soils was rapidly released as $^{14}CO_2$, but was only very slowly released as $^{14}CO_2$ from sterile soils. Losses from non-sterile soils are attributed to microbial metabolism, whereas losses from sterile soils are attributed to binding to soil components and to slow chemical degradation.

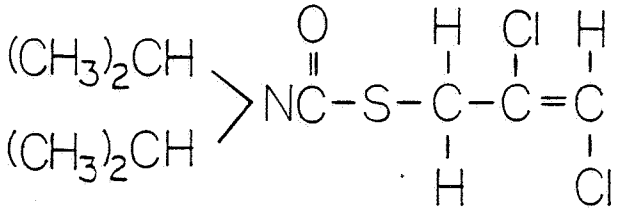
Microbiological

1. This portion of the study is scientifically valid and contains data that may be used to supplement soil metabolism data.

2. Pure cultures of fungal species, isolated from five non-sterile soils in which diallate was degraded, were capable of metabolizing diallate in liquid culture and when added back to sterile soil. Soil degradation by pure cultures was slower than degradation in liquid cultures.

MATERIALS AND METHODS:

DIALLATE, AVADEX, DATC, CP 15336



S-(2,3-dichloroallyl)-diisopropylthiocarbamate

Metabolism - Aerobic Soil

Five soils (Table 1) were treated with diallate (Avadex 40% ai, BASF, Ludwigshafen, FRG) at 1 ppm. Batches (2 kg) of sterile and non-sterile, sieved (<2 mm) soil were prepared by thoroughly mixing in diallate adsorbed on sterile talc. The sterile soils were prepared by autoclaving three times for 2 hours over a 4-6 day period. Samples were incubated in the dark at 22 C as 40-g aliquots in 125-ml cotton-stoppered flasks. Soil moisture (Table 1) was maintained constant by adding sterile distilled water as necessary. Triplicate samples were removed at 0, 1, 2, 3, 4, 6, 8, 10, and 20 weeks of incubation and extracted with benzene:isopropanol (2:1, v:v) according to the method of Smith (1969. J. Agric. Food Chem. 17:1052). Isopropanol and acidic impurities were removed with aqueous 3% sodium carbonate, the benzene layer was further cleaned up by using activated charcoal, dried over sodium sulfate, and analyzed by using electron capture GLC.

Some soil samples were incubated with carbonyl-labeled [^{14}C]diallate (Radiochemical Center, Amersham, UK); total CO_2 and $^{14}CO_2$ were monitored throughout the incubation period. Effluent gasses were passed through toluene and paraffin oil traps to remove volatilized diallate and then through methanol:ethanolamine (7:3, v:v) to trap $^{14}CO_2$. Radioactivity in trapping solutions was monitored by using LSC.

Microbiological

The metabolism of diallate was studied in pure cultures of fungi isolated from the five soil types. Those species present in high frequency and in all soils were isolated, purified, and placed in liquid culture containing diallate at 2 ppm. One species Trichoderma harzianum was also added as a pure culture to soil. Cultures were extracted for analysis according to the method of Anderson et al. (1970. J. Econ. Entomol. 63:1595).

REPORTED RESULTS:

Metabolism - Aerobic Soil

Diallate disappeared rapidly from non-sterile soils and very slowly from sterile soils indicating that the degradation was microbial in nature (Table 2). In one soil, 50% of the 2 ppm diallate dose disappeared within 1.5 weeks, in two others within 2.5 weeks, and in the remaining two within 4 weeks. In sterile soils, 54-59% of the initial dose was recovered after 20 weeks of incubation. Microbial metabolism was confirmed using carbonyl-labeled [^{14}C]diallate added to one non-sterile soil and a sterile control of the same soil. Over 25% of the 1 ppm dose was recovered as $^{14}CO_2$ from the non-sterile sample within 2 days, whereas only 8% was recovered as $^{14}CO_2$ from sterile soil in 7 days. A material balance for this experiment is given in Table 3.

Microbiological

Detection of $^{14}CO_2$ as a major metabolite under non-sterile conditions further substantiated microbial metabolism as the major degradation mechanisms. Microbial metabolism was proven by isolation of fungal species in pure culture, testing those appearing in high numbers in all test soils for diallate degradation. Species found to metabolize diallate at >20% of the applied dose (2 ppm) were Phoma eupyrina, Penicillium janthinellum, and Trichoderma harzianum. The latter species appeared to use diallate as a supplemental carbon source and was tested further by adding it to sterile soil containing diallate. Degradation occurred during 10 days of incubation (Table 4), although at a lower rate and to a lower extent than in liquid medium.

DISCUSSION:

Experimental procedures and protocols were generally well described. Metabolites other than CO_2 were not identified.

Table 1. Soil characteristics.

Soil type	pH	C (%)	Moisture[a] (%)
Brown earth	5.2	0.6	14.0%
--[b]	6.7	1.2	13.9
Brown earth	5.5	3.7	23.6
Brown podzol	5.4	1.3	11.0
Chernozem	7.5	2.3	20.8

[a]Calculated by reviewer.
[b]Unspecified.

Table 2. Disappearance of diallate from five agricultural soils.

Weeks	Diallate remaining (% of day 0)									
	Brown earth		Unspecified		Brown earth		Brown podzol		Chernozem	
	N[a]	S[b]	N	S	N	S	N	S	N	S
1	66	100	72	94	70	85	63	90	66	94
2	62	98	57	87	68	--[c]	41	88	53	93
3	43	85	53	81	52	88	32	86	42	91
4	38	82	46	83	54	83	16	80	39	95
6	28	66	30	72	43	83	13	82	31	96
8	17	62	25	75	36	72	--	--	22	90
10	18	62	28	81	31	74	9	53	14	88
20	6	54	6	59	12	69	1	57	3	62

[a]N = non-sterile.

[b]S = sterile.

[c]Not reported.

Table 3. Distribution of radioactivity from [^{14}C]diallate in soil extracts and evolved gas.[a]

Days	Fraction	[^{14}C]Diallate residues[a]	
		Sterile soil	Non-sterile soil
	Soil extract		
0	Benzene	100	100
	Aqueous	0	0
	Soil residue[b]	Tr	Tr
	Gas ($^{14}CO_2$)	0	0
	Soil extract		
7	Benzene	84.8	45.9
	Aqueous	0	0
	Soil residue	7.5	10.4
	Gas ($^{14}CO_2$)	7.7	43.7

[a]Expressed as percent of radioactivity recovered. Actual recovery was 95-100% of applied dosage.

[b]After solvent extraction.

Table 4. Degradation of diallate by a pure culture of Trichoderma harzianum.

	Recovery[a]			
	Liquid medium		Soil	
Days	Live	Sterile	Live	Sterile
0	100	100	100	100
5	46	89	84	89
10	34	65	79	90

[a]Percent of applied dose.

CASE GS 0098 DIALLATE STUDY 6 PM 04/12/82

CHEM 078801 Diallate

BRANCH EFB DISC --

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID No MRID CONTENT CAT --

Marvel, J.T., B.B. Brightwell, J.M. Malik, M.L. Sutherland, and M.L. Rueppel. 1978. A simple apparatus and quantitative method for determining the persistence of pesticides in soil. J. Agric. Food Chem. 26(5):1116-1120.

SUBST. CLASS = S.

DIRECT RVW TIME = 4½ (MH) START-DATE END DATE

REVIEWED BY: W. Spangler
TITLE: Staff Scientist
ORG: Dynamac Corp., Enviro Control Division, Rockville, MD
LOC/TEL: 468-2500

SIGNATURE: W. Spangler DATE: Sept. 24, 1982

APPROVED BY:
TITLE:
ORG:
LOC/TEL:

SIGNATURE: DATE:

CONCLUSIONS:

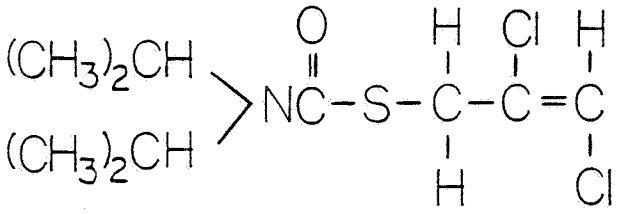
Metabolism - Aerboic Soil

1. This study is scientifically valid.

2. A simple metnod was developed to study aerobic degradation of pesticides and was used to study the rate and extent of [^{14}C]diallate metabolism in soil. Diallate degraded rapidly with a half-life of <2 weeks in Ray silt loam soil incubated at 25 C and 75% of field capacity in the dark. After 2 weeks of incubation, 7% of the 2 ppm dose was recovered as $^{14}CO_2$, 26% was volatile organics, 43% was organo-extractable, and 20% was bound to soil. At termination, 40.3% of the added radioactivity was recovered as intact parent compound.

MATERIALS AND METHODS:

DIALLATE, AVADEX, DATC, CP 15336



S-(2,3-dichloroallyl)-diisopropylthiocarbamate

An apparatus was developed to quantitate degradation of ^{14}C-labeled pesticides in soil under aerobic conditions. The apparatus consists of of a 250-ml reaction flask topped with a two-stage trapping tower. The lower portion contains a polyurethane foam plug to trap labeled volatile organics, and the upper portion contains Ascarite for trapping of $^{14}CO_2$. Trapped volatile organics are extracted from the foam plugs with methylene chloride and total radioactivity is measured by using LSC. Soils are extracted (unspecified solvent) "exhaustively", total activity determined by using LSC, and further analyzed for parent compound and degradates by using TLC and GLC. Labeled CO_2 is released from the Ascarite with acid, trapped in NaOH or phenethylamine trapping solution, and is quantitated by using LSC.

Diallate degradation was studied in the above system in Ray silt loam soil (1.2% organic matter, CEC 10.4 meq/100 g, pH 8.1, water-holding capacity 23.9%). [2-^{14}C]Diallate (9.62 mCi/mmol, >96% radiochemical purity, Monsanto Co) was added at 2 ppm to 50-g aliquots of soil as 0.1 mg of labeled material in 0.5 ml ethanol. Moisture was adjusted to 75% of field capacity, and duplicate flasks were incubated in the dark at 25 C. At 1 and 2 weeks, traps were changed, and at 2 weeks flask contents were removed for analysis as previously described.

REPORTED RESULTS:

[^{14}C]Diallate was rapidly degraded in soil under aerobic conditions. After 2 weeks incubation, 40.3% of the total dose was recoverable as parent compound. At termination of the experiment, 96.8% of the total added radioactivity was recovered as $^{14}CO_2$ (7.4%), volatile organics (26.5%), organo-extractables (42.9%), and soil bound residues (20.0%). The only degradate identified was $^{14}CO_2$.

DISCUSSION:

Degradates other than CO_2 were not identified.

CASE GS 0098 DIALLATE STUDY 7 PM 04/12/82

CHEM 078801 Diallate

BRANCH EFB DISC --

FORMULATION 12 - EMULSIFIABLE CONCENTRATE

FICHE/MASTER ID No MRID CONTENT CAT --

Anderson, J.P.E., and K.H. Domsch. 1980. Relationship between herbicide concentration and the rates of enzymatic degradation of ^{14}C-diallate and ^{14}C-triallate in soil. Arch. Environ. Contam. Toxicol. 9(3):259-268.

SUBST. CLASS = S.

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

REVIEWED BY: W. Spangler
TITLE: Staff Scientist
ORG: Dynamac Corp., Enviro Control Division, Rockville, MD
LOC/TEL: 468-2500

SIGNATURE: W. Spangler DATE: Sept. 29, 1982

APPROVED BY:
TITLE:
ORG:
LOC/TEL:

SIGNATURE: DATE:

CONCLUSIONS:

Metabolism - Aerobic Soil

1. This portion of the study is scientifically valid.

2. [^{14}C]Diallate was rapidly degraded in soil with half-lives ranging from 2 to 5 weeks at soil concentrations of 0.5-10 ppm. At 50 ppm, the half-life was 16 weeks. The only degradate detected was $^{14}CO_2$.

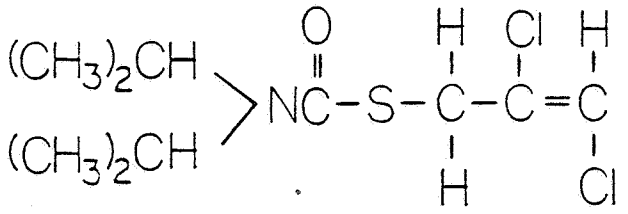
Mobility - Laboratory Volatility

1. This portion of the study is scientifically valid.

2. Approximately 2-11% of [^{14}C]diallate volatilized from soil during 30 weeks of incubation at 22 C when initially present at 0.5-10 ppm. During the same period, ~24% of a 50-ppm soil application volatilized.

MATERIALS AND METHODS:

DIALLATE, AVADEX, DATC, CP 15336



S-(2,3-dichloroallyl)-diisopropylthiocarbamate

The aerobic metabolism and laboratory volatility of [^{14}C]diallate was studied in an agricultural soil (textural characteristics were referenced). The soil (pH 5.4, 1.3% total C) was treated with diallate (Avadex EC, Monsanto Co.) to give 0.5, 1.0, 5.0, 10.0, and 50.0 ppm. Carbonyl-labeled [^{14}C]diallate (96% radiochemical purity, Radiochemical Centre, UK) was added to the formulated product to give a final concentration of 1.08 µCi/mg ai. After treatment, 40-g subsamples were incubated in 100-ml Erlenmeyer flasks fitted for the collection of volatilized pesticide and $^{14}CO_2$. The respective trapping agents were a glass wool plug coated with paraffin oil and granular soda lime, both were placed in a glass column (135 x 25 mm id) on top of the flask. Flasks were incubated in the dark at 22 ± 0.5 C for 7 days (short-term experiments) or for 30 weeks (long-term experiments). During incubation, soil moisture was maintained at ∿12.8% and traps were changed at 1, 3, and 5 days for short-term experiments; duplicate flasks were removed for analysis at 1, 3, 5, and 7 days. Traps were changed at 2-week intervals for long-term experiments; duplicate flasks were removed for analysis at 1, 4, 8, and 30 weeks.

Soil samples were extracted by shaking with benzene:isopropanol (2:1, v:v), the supernatant was decanted, and isopropanol was removed by shaking twice with aqueous 2% sodium sulfate. The benzene solutions were cleaned up with activated charcoal and dried over sodium sulfate. Each 40-g (dry weight) sample was extracted three times and the extracts pooled for analysis. The soil residue was further rinsed with 50 ml benzene, dried, combusted, and analyzed by using LSC. Volatilization traps were extracted as described above. Extracts were analyzed by using electron-capture GLC. The $^{14}CO_2$ from soda lime traps was released by acidification, retrapped in ethanolamine:methanol (3:7, v:v), and analyzed by using LSC.

REPORTED RESULTS:

Metabolism - Aerobic Soil

During short-term exposure, [^{14}C]diallate was metabolized to $^{14}CO_2$ without a lag phase. Addition of 0.5 ppm resulted in 2.4% conversion of label to $^{14}CO_2$ per day during 7 days of incubation, whereas 0.25%

conversion per day occurred at 50 ppm during the same period. During long-term exposure (30 weeks), [^{14}C]diallate was rapidly degraded in soil with half-lives of 2-5 weeks at soil concentrations of 0.5-10 ppm. At 50 ppm, the half-life was 16 weeks (Table 1). The only degradate detected was $^{14}CO_2$. After 30 weeks' incubation, 5-10% of the total radioactivity remained as unidentified bound residues and 2.7-27% remained in the soil as parent compound.

Mobility - Laboratory Volatility

[^{14}C]Diallate slowly volatilized from soil at 22 C under static laboratory conditions. During 30 weeks of incubation, a total of ∿2-11% was volatilized when [^{14}C]diallate was initially present at 0.5-10 ppm. During the same period, ∿24% of a 50-ppm soil application volatilized.

DISCUSSION:

A formulated product containing diallate (Avadex EC) was used to dilute the radiolabeled tracer.

Table 1. Volatilization, degradation, and soil binding of [^{14}C]diallate as a function of concentration.

Week	Distribution of radioactivity	[^{14}C]Diallate residues (% of recovered dose)[a] 0.5 ppm	1.0 ppm	5.0 ppm	10.0 ppm	50.0 ppm
0	Soil					
	Diallate	98.3	98.7	97.2	97.5	97.8
	Unextractable	1.7	1.0	1.4	1.0	0.6
1	Atmosphere					
	Diallate	1.2	1.7	2.6	2.7	2.8
	CO_2	19.2	16.3	8.4	6.1	5.0
	Soil					
	Diallate	66.7	74.4	81.1	85.9	89.2
	Unextractable	8.8	4.8	5.4	3.3	1.8
4	Atmosphere					
	Diallate	2.3	3.4	6.7	6.2	9.7
	CO_2	59.7	53.9	32.1	25.4	10.3
	Soil					
	Diallate	21.0	27.3	50.6	58.5	74.3
	Unextractable	16.5	13.4	6.9	6.1	2.9
8	Atmosphere					
	Diallate	1.9	3.1	8.5	9.6	12.2
	CO_2	79.2	77.8	48.9	43.2	19.4
	Soil					
	Diallate	6.7	10.5	31.5	38.4	63.0
	Unextractable	12.0	7.6	8.3	6.5	2.8
30	Atmosphere					
	Diallate	1.8	1.7	9.0	11.1	23.8
	CO_2	84.3	83.9	75.2	71.9	42.0
	Soil					
	Diallate	3.8	2.7	5.1	8.5	27.3
	Unextractable	10.0	10.4	8.7	6.7	5.1

[a]Average radioactivity recovered, in percent of applied, was 95.4 ± 2.7.

CASE GS 0098 DIALLATE STUDY 8 PM 04/12/82

CHEM 078801 Diallate

BRANCH EFB DISC --

FORMULATION 12 - EMULSIFIABLE CONCENTRATE

FICHE/MASTER ID No MRID CONTENT CAT --

Anderson, J.P.E., and K.H. Domsch. 1980. Influence of selected pesticides on the microbial degradation of ^{14}C-triallate and ^{14}C-diallate in soil. Arch. Environ. Contam. Toxicol. 9:115-123.

SUBST. CLASS = S.

DIRECT RVW TIME = 4½ (MH) START-DATE END DATE

REVIEWED BY: W. Spangler
TITLE: Staff Scientist
ORG: Dynamac Corp., Enviro Control Division, Rockville, MD
LOC/TEL: 468-2500

SIGNATURE: W. Spangler DATE: Oct. 1, 1982

APPROVED BY:
TITLE:
ORG:
LOC/TEL:

SIGNATURE: DATE:

CONCLUSIONS:

Metabolism - Aerobic Soil

1. This portion of the study is scientifically valid.

2. [^{14}C]Diallate was rapidly degraded in soil with a half-life of about 22 days at a soil concentration of 1 ppm. During 70 days incubation at 22 C, 61.3% of the added radioactivity was recovered as $^{14}CO_2$ at termination, 18.5% remained in the soil as unidentified bound residues and 12.8% was extractable from soil as parent compound.

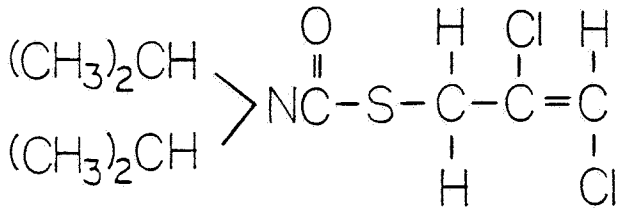
Mobility - Laboratory Volatility

1. This portion of the study is scientifically valid.

2. During 70 days of incubation at 22 C, 6.4% of applied (1 ppm) [^{14}C]diallate was volatilized from soil as the parent compound.

MATERIALS AND METHODS:

DIALLATE, AVADEX, DATC, CP 15336



S-(2,3-dichloroallyl)-diisopropylthiocarbamate

An agricultural soil (pH 5.4, 1.26% total C, unspecified textural characteristics) was sieved (<2 mm) and treated with diallate (Avadex EC, Monsanto Co.) to a final concentration of 1 ppm dry weight of soil. Carbonyl-labeled [^{14}C]diallate (96% radiochemical purity, Radiochemical Centre, UK) was added to the commercial formulation at 1.08 μ Ci/mg ai. After treatment, 40-g subsamples were incubated in 100 ml Erlenmeyer flasks fitted for the collection of volatilized diallate and $^{14}CO_2$. The respective trapping agents were a glass wool plug coated with paraffin oil and granular soda lime, both were contained in a glass column (135 x 25 mm id) on top of the flasks. Flasks were incubated in the dark at 22 ± 0.5 C and soil moisture content was maintained at 12%.

At 0, 14, 28, 35, and 70 days flasks were removed in duplicate and the contents extracted by shaking with benzene:isopropanol (2:1, v:v); the supernatant was decanted, and isopropanol was removed by shaking twice with aqueous 2% sodium sulfate. The benzene solutions were cleaned up with activated charcoal and dried over sodium sulfate. Each 40-g (dry weight) sample was extracted three times and the extracts pooled for analysis. The soil residue was further rinsed with 50 ml benzene, dried, combusted, and analyzed by using LSC. Volatilization traps were extracted as described above. Extracts were analyzed by using electron-capture GLC. The $^{14}CO_2$ from soda lime traps was released by acidification, retrapped in ethanolamine:methanol (3:7, v:v), and analyzed by using LSC.

REPORTED RESULTS:

Metabolism - Aerobic Soil

[^{14}C]Diallate was rapidly degraded with a half-life of ∿22 days. $^{14}CO_2$ was the only degradate detected. During 70 days of incubation, 61.3% of the added radioactivity was recovered as $^{14}CO_2$, 18.5% remained in the soil as unidentified bound residues, and 12.8% was extractable from soil as parent compound.

Mobility - Laboratory Volatility

During 70 days of incubation at 22 C, 6.4% of the initial dose (1 ppm) of [^{14}C]diallate was volatilized as parent compound.

DISCUSSION:

The methods and protocols were generally well described; however, complete soil characteristics were not presented. A formulated product containing diallate (Avadex EC) was used to dilute the radiolabeled tracer.

CASE GS 0098 DIALLATE STUDY 9 PM 04/12/82

CHEM 078801 Diallate

BRANCH EFB DISC

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID No MRID CONTENT CAT --

Burns, R.G., and W.P. Gibson. 1980. The disappearance of 2,4-D, diallate, and malathion from soil and soil components. Agrochem. Soils. (?):149-159.

SUBST. CLASS = S.

DIRECT RVW TIME = 3½ (MH) START-DATE END DATE

REVIEWED BY: T. Opeka
TITLE: Staff Scientist
ORG: Dynamac Corp., Enviro Control Division, Rockville, MD
LOC/TEL: 468-2500

SIGNATURE: Timothy J. Opeka DATE: Sept. 28, 1982

APPROVED BY:
TITLE:
ORG:
LOC/TEL:

SIGNATURE: DATE:

CONCLUSIONS:

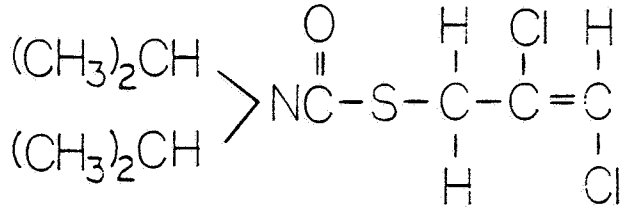
Metabolism - Aerobic Soil

1. This study is scientifically valid.

2. Diallate has a half-life of ∿70 days in non-sterile and sterile (irradiated or autoclaved) silt loam soil incubated at 25 C and 65% water-holding capacity. At higher temperatures (37 C) diallate dissipates more rapidly with a half-life of ∿25 days in non-sterile and autoclaved silt loam soil. No diallate dissipated from non-sterile or autoclaved silt loam soil incubated at 4 C.

MATERIALS AND METHODS:

DIALLATE, AVADEX, DATC, CP 15336



S-(2,3-dichloroallyl)-diisopropylthiocarbamate

Diallate (Monsanto, 95% pure; formulation unspecified) at 20 ppm (w/w) was applied to non-sterile, irradiated (gamma rays, 2.5 Mrad), or autoclaved (three 45-minute treatments at 15 PSI and 121 C) samples of a silt loam soil (16% sand, 64% silt, 20% clay, 2.2% carbon, pH 5.4, CEC 14.9 meq/100 g). The soil samples were incubated in flasks at 65% water-holding capacity and 25 C. Additional diallate-treated non-sterile and autoclaved samples were incubated at 4 and 37 C. Soil samples, at various intervals up to 70 days posttreatment, were extracted with acetone and hexane, filtered through anhydrous sodium sulphate, and evaporated almost to dryness. The extracts were methylated using a diazomethane/ether solution, reevaporated to dryness, reconstituted with methanol, and stored at 4 C until analysis. The extracts were analyzed by using a gas chromatograph equipped with an electron-capture detector. Recovery rates from soil were ∿90%.

REPORTED RESULTS:

Diallate has a half-life of ∿70 days in non-sterile, irradiated, and autoclaved silt loam soil samples incubated at 25 C. In non-sterile and autoclaved silt loam soil samples incubated at 37 C, diallate had a half-life of 25-26 days. No diallate dissipated from non-sterile and autoclaved silt loam soil samples incubated at 4 C.

DISCUSSION:

1. No attempt was made to identify degradates of diallate.

2. It was not stated whether the incubation flasks were capped or uncapped.

3. Method sensitivity was not reported.

CASE GS 0098 DIALLATE STUDY 10 PM 04/12/82

CHEM 078801 Diallate

BRANCH EFB DISC --

FORMULATION 12 - EMULSIFIABLE CONCENTRATE

FICHE/MASTER ID No MRID CONTENT CAT --

Anderson, J.P.E. 1981. Soil moisture and the rates of biodegradation of diallate and triallate. Soil Biol. Biochem. 13(2):155-161.

SUBST. CLASS = S.

DIRECT RVW TIME = 4½ (MH) START-DATE END DATE

REVIEWED BY: W. Spangler
TITLE: Staff Scientist
ORG: Dynamac Corp., Enviro Control Division, Rockville, MD
LOC/TEL: 468-2500

SIGNATURE: W. Spangler DATE: Oct. 4, 1982

APPROVED BY:
TITLE:
ORG:
LOC/TEL:

SIGNATURE: DATE:

CONCLUSIONS:

Metabolism - Aerobic Soil

1. This portion of the study is scientifically valid.

2. The degradation of [^{14}C]diallate (1 ppm) was studied as a function of soil moisture. The rate of metabolism increased as soil water content was increased within the range of 2.4 to 19.0% moisture with a corresponding decrease in half-lives from >3 weeks for ∿9 days. The rate of degradation decreased with prolonged incubation regardless of moisture content.

Mobility - Leaching

1. This portion of the study is scientifically valid.

2. [^{14}C]Diallate rapidly adsorbed to a loam soil; 99.6% of the applied dose adsorbed within 4 hours. No Freundlich K values were presented.

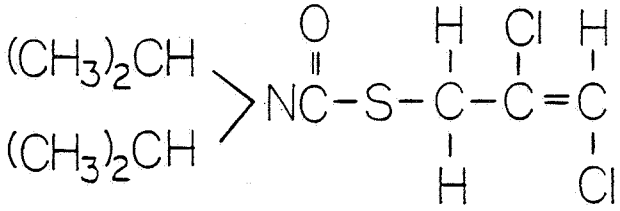
Mobility - Laboratory Volatility

1. This portion of the study is scientifically valid.

2. [^{14}C]Diallate volatilized slowly during a 3-week incubation period. Except for a very low level of volatility (0.2% of applied dose) at the lowest moisture level tested (2.4%), the rate of volatilization appeared to be constant (~3% in 3 weeks) regardless of soil moisture level.

MATERIALS AND METHODS:

DIALLATE, AVADEX, DATC, CP 15336



S-(2,3-dichloroallyl)-diisopropylthiocarbamate

Metabolism - Aerobic Soil

A loam soil (pH 5.4; sand, 41.7%; silt, 45.6%; clay, 12.7%; total C, 1.26%; and maximum water holding capacity, 36.2 g/100 g soil) was collected from a field in Germany and sieved to <2 mm. Diallate (Avadex EC, Monsanto Co.), containing carbonyl-labeled [^{14}C]diallate (96% purity, Radiochemical Centre, UK) at 1.08 µCi/mg ai, was adsorbed to talcum powder at 1 mg ai/g and added to soil (1 g talcum/kg soil) to give a final concentration of 1 ppm. The soil was used as such at 12.3% moisture or adjusted to 2.4, 9.0, 16.4, or 19.0% moisture by drying or adding water to large subsamples. Subsamples of each moisture level (40 g) were weighed in 100 ml Erlenmeyer flasks fitted to collect volatilized diallate and to trap $^{14}CO_2$, and were incubated at 22 ± 0.5 C with moisture adjustments at 3- to 5-day intervals. Duplicate flasks were removed for each moisture level after 0, 1, 2, and 3 weeks of incubation. Flask contents were extracted three times by shaking with benzene:isopropanol (2:1, v:v), and the residue rinsed with benzene. The 2.4% and 9.0% moisture soils were adjusted to 12% moisture and equilibrated prior to extraction. Isopropanol was removed from the benzene extracts with water, and combined extracts were analyzed for diallate and possible degradates by using electron-capture GLC. Bound residues were determined by using LSC following combustion of extracted soils. Trapped metabolic $^{14}CO_2$ was released by acidification, retrapped, and quantitated by using LSC.

Mobility - Leaching

Adsorption isotherms were prepared, using constant water:soil ratios, by adding 18.8 ml aqueous [^{14}C]diallate to 11.2 g of moist soil (10.0 g dry weight), shaking at 198 rpm for 4 hours, centrifuging for 20 minutes at 4,500 x G. Adsorption was determined by difference after measuring total radioactivity in duplicate 2-ml supernatant samples. Four concentrations (unspecified) were tested in duplicate for each isotherm.

Mobility - Laboratory Volatility

Diallate, volatilized from soil during aerobic metabolism studies, was trapped in a glass wool plug coated with paraffin oil. Plugs were extracted and analyzed by using the procedure described previously for analysis of diallate residues in soil.

REPORTED RESULTS:

Metabolism - Aerobic Soil

The effect of soil moisture on the rate of aerobic soil metabolism is shown in Table 1. The rate of degradation increased with increasing soil moisture but the overall rate decreased with increased incubation time. The half-lives decreased from >3 weeks to ∿9 days for soil moisture levels ranging from 2.4 to 19.0%, respectively. [^{14}C]Diallate was rapidly degraded to $^{14}CO_2$ at all moisture levels except 2.4%. Soil-bound residues appeared to be unaffected by soil moisture.

Mobility - Leaching

The adsorption isotherm for diallate is given in Figure 1 and shows a linear relationship over the range of concentrations tested; 99.6% of the applied dose adsorbed to the loam soil within 4 hours.

Mobility - Laboratory Volatility

Diallate volatilized slowly during the 3-week incubation period at 22 C (Table 1). Except for a low value (0.2% of applied dose) at 2.4% moisture, the volatilization rate appeared to be independent of soil moisture.

DISCUSSION:

1. For the adsorption experiment, no information was given about the adsorption constant (K_d) for the soil used or which adsorption equation best represented the data.

2. A mixture of analytical grade tracer and formulated product (Avadex EC) was used throughout the study.

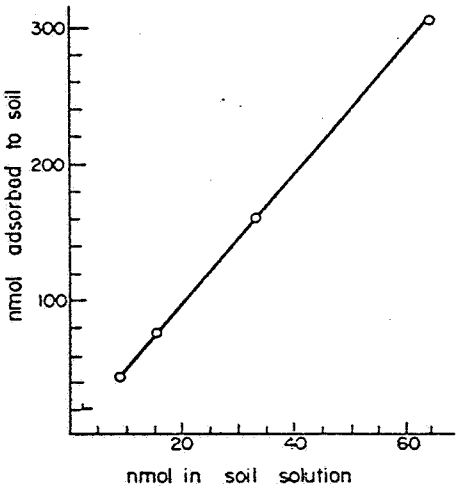


Figure 1. Adsorption isotherm for diallate in a loam soil.

Table 1. Effect of soil moisture on rates of volatilization, degradation, and binding of [^{14}C]diallate in soil.

Week	Distribution of radioactivity	[^{14}C]Diallate residues (% of applied dose) 2.4% moisture	9.0% moisture	12.3% moisture	16.4% moisture	19.0% moisture
0	Soil					
	Diallate	92.0	98.0	98.2	98.0	98.2
	Unextractable	7.0	2.0	1.7	2.0	1.8
1	Atmosphere					
	Diallate	0.0	1.6	1.8	1.7	1.7
	CO_2	0.7	15.2	17.9	21.8	27.1
	Soil					
	Diallate	84.6	69.2	67.6	63.0	55.4
	Unextractable	14.3	10.2	10.6	11.1	13.9
2	Atmosphere					
	Diallate	0.5	3.5	2.2	2.2	2.6
	CO_2	1.3	26.0	32.6	37.6	41.3
	Soil					
	Diallate	78.1	54.9	48.0	41.8	35.5
	Unextractable	19.7	14.1	13.8	15.4	19.2
3	Atmosphere					
	Diallate	0.2	3.3	3.0	2.5	2.9
	CO_2	1.6	33.7	42.7	27.6	51.0
	Soil					
	Diallate	76.1	46.5	37.3	32.2	27.2
	Unextractable	21.8	15.4	15.2	16.0	18.1

CASE 3S 0098 DIALLATE STUDY 11 PM 04/12/82

CHEM 078801 Diallate

BRANCH EFB DISC --

FORMULATION 90 - FORMULATION NOT IDENTIFIED

FICHE/MASTER ID No MRID CONTENT CAT --

Koren, E., C.L. Foy, and F.M. Ashton. 1969. Adsorption, volatility, and migration of thiocarbamate herbicides in soil. Weed Sci. 17(2):148-153.

SUBST. CLASS = S.

DIRECT RVW TIME = 4½ (MH) START-DATE END DATE

REVIEWED BY: W. Spangler and R. Schaefer
TITLE: Staff Scientists
ORG: Dynamac Corp., Enviro Control Division, Rockville, MD
LOC/TEL: 468-2500

SIGNATURE: W. Spangler R Schaefer DATE: Oct. 5, 1982

APPROVED BY:
TITLE:
ORG:
LOC/TEL:

SIGNATURE: DATE:

CONCLUSIONS:

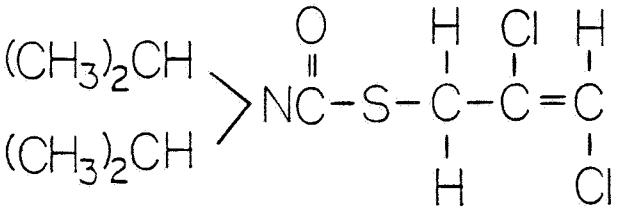
Mobility - Leaching

1. This study is scientifically valid.

2. As determined by a bioassay, diallate was immobile to slightly mobile in five soils; the rate of leaching was inversely proportional to organic matter content. When applied at 10 lb ai/A, diallate leached to 5-15 cm within 2 days after application when 55-cm columns of four soils ranging in texture from sand to loam (0.5-7.7% organic matter) were leached with ∿2-3 inches of water. Diallate was immobile in a muck soil (52% organic matter) leached with ∿4 inches of water.

MATERIALS AND METHODS:

DIALLATE, AVADEX, DATC, CP 15336



S-(2,3-dichloroallyl)-diisopropylthiocarbamate

Leaching of diallate was studied in five soil types: Staten Island peaty muck, Stockton adobe sandy loam (reported as a clay), Yolo clay loam, Hespina fine sandy loam, and washed sand. Two experiments were run in triplicate for each soil in 4.75 x 60 cm aluminum columns separated along the longitudinal axis. In the first experiment, soil was packed to a depth of 55 cm, diallate (formulation and source unspecified) was added in 55 ml water at 10 lb ai/A to the soil surface, and sufficient water was added to wet the soil columns almost to the bottom. This amounted to 200 ml for Staten Island peat muck, Yolo sandy loam, and Stockton adobe clay; 140 ml for Hespina sandy loam; and 70 ml for washed sand. The second experiment consisted of incorporating diallate into the upper 5 cm of the packed column and water was added 24 hours later. For both experiments, columns were sectioned longitudinally 48 hours after diallate application, and each half was planted with a single row (150 seeds) of barnyard grass, Echinochloa crusgalli. Fifteen days after seeding, the column halves were divided into 5-cm segments; and 10 representative plants from each segment were cut at soil level and weighed. Untreated barnyard grass served as the bioassay control.

REPORTED RESULTS:

As measured by barnyard grass bioassay, the mobility of diallate in soils varied from immobile to moderately mobile. The rate of leaching appeared to be inversely related to the CEC and organic matter content. In the Staten Island peaty muck, essentially all the diallate remained in the upper 1 cm of soil after 45 hours. In the Stockton adobe sandy loam leaching occurred to 10 cm, to 15 cm in Yolo clay loam, to 5 cm in Hesperia sandy loam, and to 15-cm in washed sand. No difference in mobility was observed between surface treatment and when diallate was incorporated in the upper 5 cm soil layer.

DISCUSSION:

The potential of diallate to leach could not be fully assessed from the data presented in this study because only a minimal amount of water (~2-4 inches) was applied to the soil columns.

Table 1. Soil characteristics.

Soil	Mechanical analysis (%)			Organic matter (%)	CEC (meq/100 g)	pH	Water retention (% at 1/3 atm)
	Sand	Silt	Clay				
Staten Island peaty muck	62.4	30.4	7.2	51.8	68.3	5.3	49.0
Stockton adobe sandy loam[a]	62.4	26.4	11.2	7.7	37.5	6.4	18.9
Yolo clay loam	33.2	38.8	28.8	3.3	22.0	7.5	16.0
Hesperia sandy loam	68.4	26.4	5.2	1.7	8.5	7.5	8.0
Washed sand	94.2	3.8	2.0	0.5	3.0	7.1	4.8

[a]Reported as a clay.

CASE GS 0098 DIALLATE STUDY 12 PM 04/12/82

CHEM 078801 Diallate

BRANCH EFB DISC --

FORMULATION 01 - TECHNICAL CHEMICAL

FICHE/MASTER ID 00002536 CONTENT CAT --

Grover, R. 1974. Adsorption and desorption of trifluralin, triallate, and diallate by various adsorbents. Weed Sci. 22(4):405-408. Also In unpublished submission received on unknown date under 1471-79; submitted by Elanco Products Co., Div. of Eli Lilly and Co., Indianapolis, IN; CDL:221991-C.

SUBST. CLASS = S.

DIRECT RVW TIME = 3½ (MH) START-DATE END DATE

REVIEWED BY: W. Spangler
TITLE: Staff Scientist
ORG: Dynamac Corp., Enviro Control Division, Rockville, MD
LOC/TEL: 468-2500

SIGNATURE: W. Spangler DATE: Oct. 6, 1982

APPROVED BY:
TITLE:
ORG:
LOC/TEL:

SIGNATURE: DATE:

CONCLUSIONS:

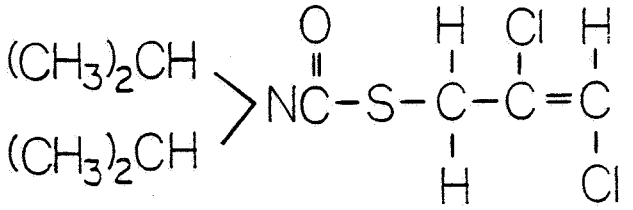
Mobility - Leaching

1. This study is scientifically valid.

2. Diallate was strongly adsorbed to peat moss (Freundlich K = 1,080).

MATERIALS AND METHODS:

DIALLATE, AVADEX, DATC, CP 15336



S-(2,3-dichloroallyl)-diisopropylthiocarbamate

Various adsorbents (0.2-1 g, but only peat moss was studied for diallate) were placed in 25 ml ground-glass stoppered tubes containing 10 ml of diallate (technical, Monsanto Co.) at 0, 4, 6, 8, or 10 ppm. Stoppered tubes were equilibrated by shaking at 30 rpm for 24 hours at 25 ± 1 C. After shaking, tubes were centrifuged at 10,000 rpm for 10 minutes, and 5-ml aliquots were extracted by shaking with 5 ml benzene. The benzene layer was dried over anhydrous sodium sulfate and analyzed by using electron capture GC. The difference between initial and final equilibrium concentrations of diallate was assumed due to adsorption. Adsorption isotherms were compared using the Freundlich equation.

REPORTED RESULTS:

Adsorption isotherms were prepared for adsorption of diallate to peat moss; diallate was strongly adsorbed to peat moss (K = 1,080; n = 0.67).

DISCUSSION:

1. Experimental procedures and protocols were acceptable. Although not performed with field soils, the experimental results indicate that diallate will be immobile in peaty soils.

2. Data were apparently not reported for adsorption of diallate on kaolinite and montmorillonite clays. Freundlich K and n values of "0" and "-", respectively, were presented. Since a Freundlich K of 0 for both clays is highly unlikely, it is assumed that adsorption experiments were not conducted with these clays for diallate.

CASE GS 0098 DIALLATE STUDY 13 PM 04/12/82

CHEM 078801 Diallate

BRANCH EFB DISC SPECIAL ORDER

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID 05021762 CONTENT CAT --

Ebing, W., and I. Schuphan. 1979. Studies on the behavior of environmental chemicals in plants and soil quantitatively investigated in closed cultivating systems. Ecotoxicol. Environ. Safety 3(2):133-143.

SUBST. CLASS = S.

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

REVIEWED BY: T. Opeka
TITLE: Staff Scientist
ORG: Dynamac Corp., Enviro Control Division, Rockville, MD
LOC/TEL: 468-2500

SIGNATURE: Dorothy J. Opeka DATE: Sept. 29, 1982

APPROVED BY:
TITLE:
ORG:
LOC/TEL:

SIGNATURE: DATE:

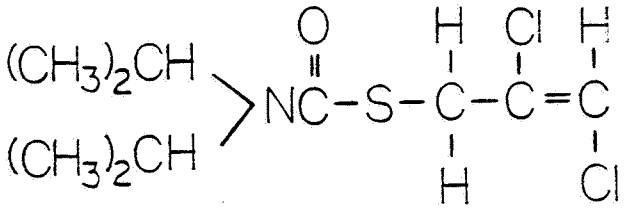
CONCLUSION:

Confined Accumulation - Rotational Crops

This study cannot be validated because the analytical method employed was not described or referenced.

MATERIALS AND METHODS:

DIALLATE, AVADEX, DATC, CP 15336



S-(2,3-dichloroallyl)-diisopropylthiocarbamate

Sandy loam soil (characteristics unspecified) was placed into glass containers, sown to sugar beets, and treated with carbonyl-labeled [^{14}C]diallate (source, formulation, purity, and application rate unspecified). The soil samples were incubated at 24 ± 3 C, 12% water capacity, and 20,000 lux illumination (12 hour on/off cycle) for 195 days. Volatile components were trapped in solutions of ethylene glycol monomethyl ether and ethanolamine. The amount of radioactivity was determined in sugar beets, soil, trapped volatile components, condensation water, and acetone and water rinses. The method of extraction and quantification of ^{14}C residues was not reported.

REPORTED RESULTS:

Approximately 98.8% of the applied radioactivity was recovered at the end of the experiment. Most of the applied radioactivity was recovered from soil (~47%) and plant (36.5%) samples, or as $^{14}CO_2$ (13%).

DISCUSSION:

1. The method of extraction and quantification of ^{14}C residues was not presented.

2. The rate of application was not specified for [^{14}C]diallate.

CASE GS0098 DIALLATE STUDY 14 PM 04/12/82

CHEM 078801 Diallate

BRANCH EFB DISC --

FORMULATION 12 - EMULSIFIABLE CONCENTRATE

FICHE/MASTER ID 00067388 CONTENT CAT--

Dubelman, S., S.A. Adams, D.D. Arras, D.G. Hanson, and R. Lauer. 1980. Applicator exposure study with Avadex emulsifiable concentrate herbicide using closed system tank fills: preliminary results: Report No. MSL-1401. Interim report. Unpublished study received Dec. 29, 1980 under 524-124; submitted by Monsanto Co., Washington, D.C.; CDL:243995-A.

FICHE/MASTER ID 00071162 CONTENT CAT --

Adams, S.A.; S. Dubelman, D.D. Arras, D.G. Hanson, and R. Lauer. 1981. Applicator exposure study with Avadex emulsifiable concentrate herbicide using closed-system tank fills: Report No. MSL-1454. Final report. Unpublished study received Feb. 12, 1981 under 524-124; submitted by Monsanto Co., Washington, D.C.; CDL:244356-A.

SUBST. CLASS =

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

REVIEWED BY: W. Spangler
TITLE: Staff Scientist
ORG: Dynamac Corp., Enviro Control Division, Rockville, MD
LOC/TEL: 468-2500

SIGNATURE: W. Spangler DATE: Oct. 7, 1982

APPROVED BY:
TITLE:
ORG:
LOC/TEL:

SIGNATURE: DATE:

CONCLUSIONS:

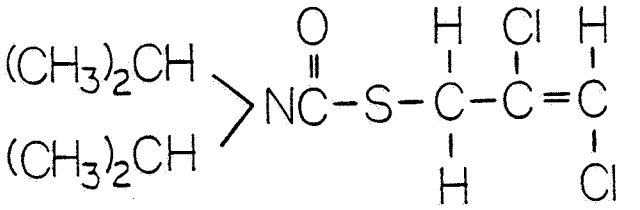
Exposure

1. This study is scientifically valid.

2. Operator exposure to diallate during tank fill operations using three closed-transfer systems was minimal. Inhalation exposure ranged from <0.18 to 1.0 $\mu g/m^3$. Diallate was not detected on cotton gloves (<0.061 $\mu g/cm^2$) or on the head, neck, and upper torso (<0.005 $\mu g/cm^2$) of operators. Equal operator protection was provided by the Chemprobe, Protect-O-Loader, and Chemductor systems tested.

MATERIALS AND METHODS:

DIALLATE, AVADEX, DATC, CP 15336



S-(2,3-dichloroallyl)-diisopropylthiocarbamate

Three commercially available closed-system transfer systems (Protect-O-Loader, Chemprobe, and Chemductor) were evaluated for operator exposure during use. The systems utilized one of two basic designs; the probe type or the cannister type. The probe type consists of a cylindrical probe, very similar to a beer keg tap, used to penetrate the seal of a 5-gallon herbicide can through the plastic spout. A transfer pump transfers the contents directly into the spray tank. When empty, the can is rinsed directly to the tank by attaching a hose to a valve on the probe. The cannister type consists of a container slightly larger than the herbicide can in which the 5-gallon can is placed. A metal punch on the bottom of the cannister punctures the can for pumping. Closing the cannister lid punctures the vent tube in the top of the can. The can is rinsed by a valve attached to a hose and rinsing occurs through the vent tube.

The transfer systems were field-evaluated during spraying operations on a farm in Kindred, ND. During transfer of diallate (Avadex EC, Monsanto Co.), air samples were collected on 4-inch diameter 2-inch thick polyurethane foam plugs using high volume samplers. Volume was adjusted to ∿50 times normal breathing rate, and air was sampled close to the operators' face throughout the fill operation. A second type of personal sampler was also used which used silica gel in a glass tube as the collection medium. After collection, samples were placed in cans and frozen until analysis.

Herbicide exposure to skin and clothing was monitored with 12 ply, 4 x 4-inch gauze pads either on the disposable coveralls or on the applicators' body. Areas monitored were top of head, forehead, shoulder, chest, back, thigh, right bicep, left forearm, and ankle. Skin patches under clothing were placed on the right forearm, left bicep, and ankle. Dermal exposure to hands was monitored by placing cotton gloves between the hands and neoprene gloves. All pads and gloves were prewashed in nanograde acetone (NG) and NG hexane prior to use. After exposure, samples were stored frozen in cans until analysis. Check samples and fortified runs were performed to verify samples and analytical methodology. In order to produce fortified samples, sample matrices were spiked with microliter quantities of diallate standards.

Polyurethane foam plugs, gauze pads, and cotton gloves were extracted for analysis with hexane. The extracts were concentrated, purified by column chromatography, reconcentrated, and analyzed by using electron-capture GLC.

To increase air volume sampled by personal samplers, two units were run in parallel (two samplers), and the silica gel from both were combined for analysis. The silica gel was extracted with 10% ethyl acetate in hexane, the extracts concentrated, purified by column chromatography, reconcentrated, and analyzed by using electron-capture GLC. The detection limits of the method were 0.18 $\mu g/m^3$ for polyurethane foam plugs, 1.0 $\mu g/m^3$ for silica gel tubes, 0.005 $\mu g/cm^2$ for gauze pads, and 0.06 $\mu g/cm^2$ for gloves.

REPORTED RESULTS:

A series of laboratory checks and fortification studies were performed to validate methodology. Results using fortified air samples indicated recoveries of 103 and 81%, respectively, for polyurethane foam plugs and silica gel tubes. The recovery efficiencies for gauze pads and gloves were 93 and 98%, respectively. The results of field exposure studies, given in Table 1, indicated a low level of exposure in air during closed system tank fill operations. Inhalation exposure (foam plugs and silica gel tubes) ranged from <0.18 to 1.00 $\mu g/m^3$. Dermal desposition was non-detectable for gloves ($< 0.06 \mu g/cm^2$) and for inner and outer clothing patches ($<0.005 \mu g/cm^2$). Only thigh and ankle samples showed small measurable recoveries. Equal operator protection was indicated for all three systems listed.

DISCUSSION:

Experimental procedures and protocols were well described. Measurements were made under conditions where exposure would be expected to be minimal (pesticide transfer using a closed system).

Table 1. Operator exposure during closed system transfer of diallate.

Measurement	Sample source	Test system[a] 1[b]	2[c]	3[d]
Concentration in air ($\mu g/m^3$)	Polyurethane foam	<0.19 0.25	0.66 0.35	<0.18 <0.22
	Silica gel	<1.00 <1.00	<1.00 <1.00	<1.00 <1.00
Dermal deposition ($\mu g/cm^2$)	Hands	<0.061	<0.061	<0.061
	Head	<0.005	<0.005	<0.005
	Forehead	<0.005	<0.005	<0.005
	Shoulder	<0.005	<0.005	<0.005
	Chest	<0.005	<0.005	<0.005
	Back	<0.005	<0.005	<0.005
	Thigh	<0.066	<0.005	<0.012
	Forearm (under)	<0.005	<0.005	<0.005
	Forearm (outer)	<0.005	<0.005	<0.005
	Bicep (under)	<0.005	<0.005	<0.005
	Bicep (outer)	<0.005	<0.005	<0.005
	Ankle (under)	<0.005	<0.006	<0.005
	Ankle (outer)	<0.005	<0.005	<0.017

[a]Values are averages of three replicates.

[b]Protect-O-Loader system.

[c]Chemprobe system.

[d]Chemductor system.

CASE GS 0098 DIALLATE STUDY 15 PM 04/12/82

CHEM 078801 Diallate

BRANCH EFB DISC 30 TOPIC 0505

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID 05021883 CONTENT CAT 01

Neururer, H. 1972. Studies on the behavior of herbicides in the soil: II. Bodenkultur 23(2):138-172.

SUBST. CLASS = S. OTHER SUBJECT DESCRIPTORS PRIM: -20-2000

DIRECT RVW TIME = 5½ (MH) START-DATE END DATE

REVIEWED BY: T. Opeka
TITLE: Staff Scientist
ORG: Dynamac Corp., Enviro Control Division, Rockville, MD
LOC/TEL: 468-2500

SIGNATURE: Timothy J. Opeka DATE: Oct. 5, 1982

APPROVED BY:
TITLE:
ORG:
LOC/TEL:

SIGNATURE: DATE:

CONCLUSIONS:

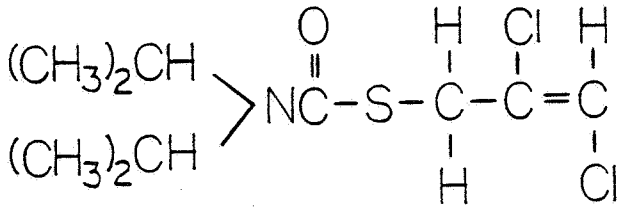
Field Dissipation - Terrestrial

1. This study is scientifically valid.

2. Diallate phytotoxic residues persisted for 2-4 months in two Austrian soils treated with diallate at 4 kg/ha.

MATERIALS AND METHODS:

DIALLATE, AVADEX, DATC, CP 15336



S-(2,3-dichloroallyl)-diisopropylthiocarbamate

In Austria, diallate (source, formulation, and purity unspecified) was applied at 4 kg/ha to field plots at the Fuchsenbigl and Petzenkirchen test stations. The soils at both test stations contained ∿2.5% humus. Soil samples were collected at 0.5, 1, and 2 weeks and at 1, 1.5, 2, 2.5, 3, 4, 5, 6, 7, 8, and 12 months posttreatment. The samples were taken to a greenhouse and sown with oats to determine the persistence of diallate phytotoxic residues.

REPORTED RESULTS:

Diallate phytotoxic residues persisted for 3, 4, and 3 months in the 1967-68, 1968-69, and 1969-70 growing seasons, respectively, at the Fuchsenbigl test station. The respective values for the Petzenkirchen test station were 2, 4, and 3 months.

DISCUSSION:

1. Several portions of the study were not reviewed because they pertained to treated crops or provided an insufficient amount of information to permit evaluation. Data Tables 1-11 were cited in the text of the study but were not presented. Soil sampling depth was not reported.

2. No attempt was made to determine the sensitivity of the oat bioassay. The bioassay method is non-specific and inadequate to distinguish between residual diallate and its degradation products.

CASE GS 0098 DIALLATE STUDY 16 PM 04/12/82

CHEM 078801 Diallate

BRANCH EFB DISC --

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID No MRID CONTENT CAT --

Smith, A.E., and B.J. Hayden. 1976. Field persistence studies with eight herbicides commonly used in Saskatchewan. Can. J. Plant Sci. 56(3):769-771.

SUBST. CLASS = S

DIRECT RVW TIME = 3 (MH) START-DATE END DATE

REVIEWED BY: T. Opeka
TITLE: Staff Scientist
ORG: Dynamac Corp., Enviro Control Division, Rockville, MD
LOC/TEL: 468-2500

SIGNATURE: Timothy J. Opeka DATE: Sept. 28, 1982

APPROVED BY:
TITLE:
ORG:
LOC/TEL:

SIGNATURE: DATE:

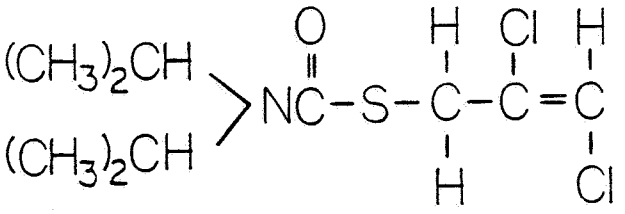
CONCLUSION:

Field Dissipation - Terrestrial

This study is scientifically invalid because of inadequate soil sampling protocols including no determination of day 0 postapplication diallate levels in soil.

MATERIALS AND METHODS:

DIALLATE, AVADEX, DATC, CP 15336



S-(2,3-dichloroallyl)-diisopropylthiocarbamate

Diallate (technical grade; source and purity unspecified) was applied at 1.7 kg/ha to Regina heavy clay (pH 7.3, 4.2% organic matter), Jameson sandy loam (pH 6.2, 3.2% organic matter), and Melfort silty loam (pH 6.7, 11.7% organic matter) field plots (20 x 20 cm) in Saskatchewan, Canada. Diallate was applied in May of 1972, 1973, and 1974. The experimental design included three replications. Soil samples were collected from depths of 1-5 cm and 5-10 cm at 5, 12, and 17 months after treatment in 1972 and 1973, and at 5 months after treatment in 1974. The samples were air-dried and ground, and subsequently extracted and analyzed by using the gas chromatographic method of Smith (1975. Pages 266-270, In E. Coulston and F. Korte, eds. Environmental quality and safety. Supp. Vol. 3 G. Thieme, Stuttgart).

REPORTED RESULTS:

Diallate dissipated to below detectable levels in the upper 5 cm of sandy loam, clay, and silty loam soils within 5 months after each of three annual applications at 1.7 kg/ha. Less than 2% of the applied diallate was recovered from the 5- to 10-cm depth of any test soil.

DISCUSSION:

1. Method recovery levels and detection limits were not provided.

2. Meteorological data were not reported.

3. Soil sampling intervals were inadequate to establish decline curves for diallate because day 0 postapplication diallate levels in soil were not determined and diallate levels were below detection at the first sampling interval (5 months postapplication). Therefore, neither the application rate nor the ability of the analytical method to detect diallate can be confirmed.