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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY WASHINGTON, D.C. 20460

OFFICE OF PESTICIDES AND TOXIC SUBSTANCES

MAR 28 1588

MEMORANDUM

SUBJECT:

Diazinon Registration Standard - EAB Science Chapter

and Data Tables.

TO:

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Attached is the EAB Registration Standard Science Chapter and the Exposure Assessment Data Requirements Table.

The data summarized in this Registration Standard fulfill the photodegradation on soil, the aerobic, anaerobic and aquatic anaerobic soil metabolism. The leaching and hydrolysis data requirements are only partially fulfilled.

The full potential of Ground Water contamination cannot be assessed without additional leaching and field dissipation data. However, the following observations are made based on the available data reported in more details in the Executive Summary of the EAB Science Chapter:

Diazinon degraded under aerobic, anaerobic, anaerobic aquatic and sterile soil conditions with the half-lives of less than 46 days. Degradation occurred at a much faster rate on soil exposed to sunlight. Preliminary hydrolysis data indicate that diazinon is stable with respect to hydrolysis at pH 7 & 9 but hydrolyzes in non-sterile water of pH 5.

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Oxypyrimidine, the primary degradate of diazinon in soil, is also formed under photolysis and hydrolysis conditions. Oxypyrimidine is more persistent in soil than the parent diazinon and is more mobile than diazinon. Therefore, oxypyrimidine poses diazinon. Oxypyrimidine is mobile and contaminate ground water than of sandy and sandy loam soil columns. A secondary degradate of oxypyrimidine was identified in the aerobic soil metabolism data differing from oxypyrimidine only by an alcohol group. Under anaerobic aquatic conditions these degradates are most likely to accumulate, persist and leach.

The potential leaching of diazinon and its two major degradates should be addressed by field dissipation studies. The field dissipation studies must include sampling to sufficient depths, and a two feet residue free zone (non-detectable residues) must be established below the deepest point of residue movement. The analytical method should be very sensitive, preferably at the 10 ppb level, to address the extent of leaching. Interim results of these for assessment. Detectable residues moving beyond the three feet depth might also trigger a small-scale prospective ground-water pattern under conditions where leaching is most likely to be observed.

Additional Reentry, Human Exposure and Spray Drift data are needed before a more complete assessment can be made. This data will address Human Exposure concerns with poisoning incidents in homes and fields. Home poisoning is also addressed in the appendix of the EAB Science Chapter. Also, there are ecological issues associated with use on golf courses.

Akiva D. Abramovitch, Ph.D., Chemist Review Section #1, EAB/HED (TS-769C)

Attachment CC: HED Branches

DIAZINON

Final Report

Task 1: Review and Evaluation of Individual Studies

Task 2: Environmental Fate and Exposure Assessment

Contract No. 68-02-4250

JUL 22 1986

Submitted to: Environmental Protection Agency Arlington, VA 22202

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

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Diazinon is an insecticide/acaricide/nematicide registered for use on a variety of terrestrial food crop (field, vegetable, and orchard crops), terrestrial nonfood crop (tobacco, ornamentals and forest trees), terrestrial noncrop (rights-of-way, ditch banks, etc.), greenhouse food crop and nonfood crop, domestic outdoor, aquatic food crop (cranberry and water cress), forestry, and indoor (domestic, commercial, and industrial) sites. Of the total diazinon applied in the United States -10-18% was used on fruits and nuts, $\sim 4-10\%$ was used on field and vegetable crops, $\sim 3-4\%$ was used on livestock, -40-42% was used by homeowners, and -26-40% was used in commercial and industrial sites. Application rates range from 0.1-19.5 1b ai/A or 0.008-0.3 1b ai/gal for foliar, soil, and turf treatments; 0.42-1.67 oz ai/bu for seed treatments; 1-3.85 g ai/tree for stem and trunk treatments; 0.03-1.0% ai sprays for indoor use; 11 or 15% ai for impregnated pet collar use; and up to 100 lb ai/A for garbage dump and manure treatments. Diazinon may be formulated with piperonyl butoxide, pyrethrins, zineb, rotenone, maneb, sulphur, captan, copper sulfate, folpet, lindane, benfluralin, chlorothalonil, malathion, dicofol, dinocap, methoxychlor, tetrachloroethylene, methylated naphthalenes, ronnel, MGK 264, aromatic naptha, lethane 386, lethane 60, d-trans allethrin, resmethrin, sulfoxide, oil of citronella, and mineral spirits. Single active ingredient formulations consist of 1-33.34% D; 0.46-14.3% G; 25, 40, and 50% WP; 2 lb/gal and 1% Mcap; 10-39% Impr; 0.33-6 lb/gal and 3-48% EC; 4 lb/gal SC/L; 0.42-10% RTU; 1 and 5% PrL; and 1% PrL Mcap. Diazinon is generally applied foliarly or as a soil treatment using ground or air equipment. Applicators need not be certified or under the direct supervision of applicators certified to apply diazinon.

No federal reentry intervals have been established; however, California has established a reentry interval of 5 days.

EC, purity unspecified, source unspecified] was added to each buffer solution at 10 or 30 ppm. The flasks were incubated in the dark at 30°C. Samples were taken at 0, 7, 14, 21, and 31 days. Samples containing the MCAP formulation of diazinon were extracted with acetonitrile (ultrasonic (5 ml) were added and the pH was adjusted to 9.5-10. This solution was by GC equipped with a flame photometric detector. Samples containing the EC formulation were analyzed similarly except the ultrasonic acetonitrile extraction was deleted.

REPORTED RESULTS:

Diazinon in aqueous solution was most stable at neutral pH and most labile at acidic pH (Table 1). At pH 5 the half-lives for the EC and MCAP formulations were 0-7 and >31 days, respectively. At pH 7 a half-life was not reached in 31 days for either formulation. At pH 9 diazinon as the EC formulation had a half-life of 21 days; a half-life was not obtained with the MCAP formulation (>31 days).

DISCUSSION:

- Sterility was not maintained during the experiment; therefore, degradation cannot be attributed solely to hydrolysis.
- The purity of the test substance was not specified; pure active ingredient should be used.
- 3. No precautions were taken to minimize loss of the test substance by volatilization.
- A material balance was not provided, and degradates were not identified.

Table 1. Diazinon (ppm)a in aqueous solutions buffered to pH 5, 7, and 9 treated with diazinon at 10 and 30 ppm and incubated in the dark at 30°C for up to 31 days.

			Samplin	ng interval	(days)	
Concentration (ppm)	рН	0	7	14	21	31
		Microencap	sulated for	mulation	•	
10	5	6.60	5.15	4.60	4.00	3.65
	7	7.60	6.85	7.00	6.95	6.70
	9	7.40	6.95	7.45	7.65	8.05
30	5	23.10	16.50	11.40	13.30	14.30
	7	24.20	24.45	24.50	24.45	25.35
	9	28.20	25.25	26.80	27.50	26.25
•		EC	formulatio	<u>n</u>		
10	5	9.00	0.80	0.11	0.01	ND ^b
	7	8.80	7.45	8.15	6.30	4.90
	9	9.00	7.10	5.45	4.65	3.30
30	5	26.70	3.15	0.40	0.04	ND
	7	28.10	25.60	20.75	20.35	17.05
	9	29.10	21.30	18.00	14.55	9.65

a Figures represent the average of duplicate samples.

h Not detectable; detection limit not specified.

CASE GS0238 DIAZINON STUDY 2 CHEM 057801 Diazinon BRANCH EAB DISC --FORMULATION 00 - ACTIVE INGREDIENT FICHE/MASTER ID 00153230 CONTENT CAT 01 Blair, J. 1985. Photodegradation of diazinon on soil: Study No. 6015-208. Unpublished study prepared by Hazleton Laboratories America, Inc. 130 p. SUBST. CLASS = S. DIRECT RVW TIME = 8 (MH) START-DATE REVIEWED BY: J. Blake
TITLE: Staff Scientist ORG: Dynamac Corp., Rockville, MD TEL: 468-2500 APPROVED BY: A. Abramovitch TITLE: Chemist ORG: EPA TEL: (703) 557-1,392 SIGNATURE:

CONCLUSIONS:

Degradation - Photodegradation on Soil

- 1. The natural sunlight data from this study are acceptable and along with the data in Study 3 they fulfill EPA Data Requirements for photodegradation on soil.
- [14C]Diazinon (99% pure) applied to sandy loam TLC plates at levels of 7, 33 and 51 ppm, degraded with a half-life of 37.4 hours after exposure to natural sunlight. The half-life of the dark control sample was 926 hours. The degradate, the expypyrimidine, was detected at the highest concentration (19.6% of the applied radioactivity) after 13.5 hours of sunlight exposure. The distribution of radiolabeled material near the half-life point (35.5 hours vs. 37.4 hours for the half-life) was 20.7% in soil bound residues (some of which was the expypyrimidine), 24.4% expypyrimidine and 39.7% identified residues and carbon diexide (0.5%). The total radioactive material balance was 87-89% at the 0 hour to above 84% at all other experimental points.

MATERIALS AND METHODS:

A horizontal band (about 1 cm) of silica was removed from silica gel TLC plates 1.5 cm from one end, and three vertical channels were cut in the

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A slurry made from water and California sandy loam soil (54.8% sand, 29.4% silt, 15.8% clay, 2.0% organic matter, CEC 15 meq/100g, field moisture capacity 36.05%, pH 5.4) was applied to the 1 cm band and allowed to dry. The soil on the plates was spotted with ring labeled [2-14C]diazinon (specific activity 24.5 microCi/mg, 99% pure, Ciba-Geigy Corp.) in ethanol at 7, 33, or 51 ppm. Five plates were placed 4 cm below two 20-watt Chroma 50 lamps, (F20T12/C50, GE) with wavelengths of 390-750 mm (Figure 1) for a light intensity of about 4800 lumens/m2. The holding chamber was tinted to exclude extraneous light and was connected in series to an ethylene glycol trap and an ethoxyethanol:ethanolamine (50:50, v/v) trap for collection of volatile organics and carbon dioxide, respectively. Air was pulled through the system. The temperature in the chamber was 29-30°C. Five plates were exposed to natural sunlight in October in Wisconsin at a light intensity of 30,000 to 48,000 lumens/m². These plates were stored in the dark between periods of exposure. Five control plates were kept in the dark at about 23°C in a foil covered tray. The traps and the plates in the artificial light chambers were sampled at 0, 42, 90, 141, and 210 hours; those exposed to sunlight were sampled after 0, 5, 13.5, 21, 35.5, and 58.5 hours of exposure; and dark controls were sampled at 0, 24, 48, 120, 168, and 264 hours.

For photoproduct identification five TLC plates prepared with soil (as above) were spotted with [14C]diazinon in ethanol at 33 ppm, and another five plates spotted with [14C]diazinon in hexane at 33 ppm. The plates were exposed to natural sunlight for 26.5 or 58.5 hours.

After exposure the plates were developed with toluene:chloroform: ethanol: formic acid (8:8:2:1), dried, and the [14C]radioactivity was measured with a TLC linear analyzer. The radioactivity in the diazinon band on the TLC plate was divided by the total radioactivity measured on the strip. For the identification of major photoproducts, the plates were extracted with methanol, and cochromatographed with the nonradioactive oxypyrimidine (see Appendix for structure) on HPLC plates using toluene:chloroform:ethanol:formic acid (8:8:2:1) or ethylether: acetone: chloroform (1:3:16). The nonradioactive oxypyrimidine was visualized by fluorescent quenching and UV light, and the radioactivity was visualized by autoradiography. Minor photoproducts were quantified by scraping zones on the autoradiographed plates, mixing the scrapings with water and analyzing by LSC. Soil from the plates was exidized and the trapped 14002 was analyzed by LSC. To characterize polar photoproducts, sunlight exposed plates were developed with toluene:chloroform:ethanol:formic acid (8:8:2:1), scraped, extracted first with methanol, then with water, concentrated, and cochromatographed with the nonradioactive oxypyrimidine in the above solvent system. Radioactivity in the traps connected to the exposure chamber was quantified by LSC. To determine the material balance, total radioactivity on a plate was measured by scraping the radioactive silica zones, combining the scrapings, and analyzing by LSC. The soil was oxidized and subjected to LSC.

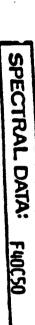
REPORTED RESULTS:

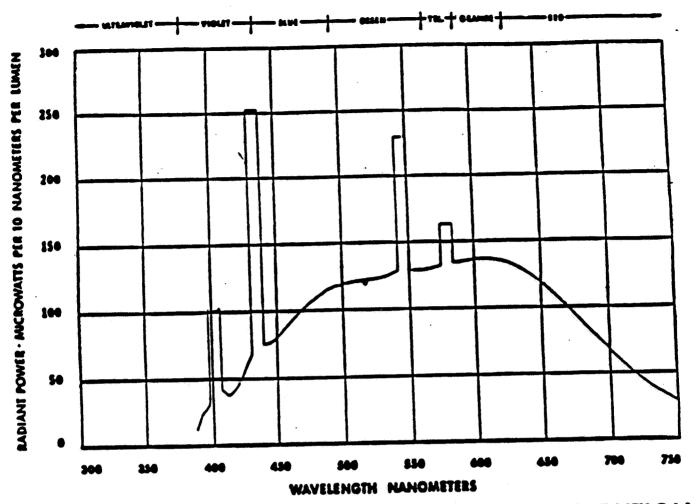
[14C]Diazinon on sandy loam soil degraded when exposed to natural sunlight with a half-life of 37.4 hours. The major degradate, the oxyprimidine, obtained maximum concentrations of 19.60% (13.5)

total of 0.5% of applied [14C] radioactivity. [14C] Radioactivity not identified ranged from 0.40 to 7.81% of applied under natural light exposures. Bound [14C] radioactivity accounted for up to 30.05% of applied under natural light.

DISCUSSION:

- 1. The natural sumlight photolysis study is sufficient to satisfy EPA Data Requirements for Registration. Therefore, the photolysis data under artificial light were not considered, particularly since sunlight conditions were not simulated, a fact which makes the study unacceptable.
- 2. Degradation of diazinon upon exposure to sunlight having intensity of 30,000-48,000 limen/m² in the month of October was much faster (half-life of 37.4 hr) than observed in darkness (half-life of 264 hr).





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Figure 1. Wavelength spectra of artificial light (two 20-watt Chroma 50 lamps) as presented in hardcopy.

natural sunlight exposure.

Time			14-C	Recovered (DPM) and I	of radioactiv	(i+v ===1: ::
(hours)) Plat	e ID	Origin	Zone I	Diazinon	Diffuse	Total 14-0
5	208-5-1		6936 16.06%	4543 10.49%	34643 80.01%	226 0.52%	46368c
	208-5-1		4883 11.28%	4391 10.14%	28439 65.68%	151 0.33%	89.24% 37866 87.43%
13.5	208-5-1		3893 8.99%	3367 8.24%	30163 69.67%	142 0.33%	37767 87.22%
4 4 6 (1	208-5-2	•	6842 15.80%	9311 21.30%	17803 41.12%	121	34077 78.70%
	208-5-2	CHO 2	7681 17.74%	8302 19.17%	22828 52.72%	128 0.30%	18939 89.93 %
1	208-5-2	CHU 3	7455 17.22%	7861 18.15%	22758 52.56%	310 0.72%	18184 88.65%
-	208-5-3	CHO 1	10858 25.08%	5652 13.05%	19796 45.72%	134 0.31%	36440 84.16%
		CHO 2	11212 25.89%	4192 9.68%	20145 46.52%	3295 7.61%	38844 89.71%
•5		CHO 3	11679 26.97%	3117 18.75%	18089 41.78%	3133 7.24%	41018 94.73%
••		CHO 1	14870 34.34%	6650 15.36%	15400 33.57%	971 2.24%	57891 87.31%
	208-5-4	CHO 2	(b)				
	208-5-4	CHO 3	11159 25.77%	4770 11.02%	16300 37.64%	5738 13.37%	18017 87.80%

a Origin: Soil hand.

Zone I: Portions of silica strip associated with nzypyrimidine.
Niazinon: Portions of silica strip associated with parent compound.
Diffuse: Portions of silica strip not associated with any compound.

b Plate 208-5-4, CHO 2 was used in a preliminary investigation. Ouantitation not possible.

C Soil hand number one fortified with 51960 dpm.

Table 2. Material balance of [14C]radioactivity (% of applied)a in soil on TLC plates exposed to natural sunlight or not exposed, as analyzed by LSC.

ampling nterval hours)	Boundb	Oxypyrimidinec	Diazinon	niffused	Total
	<u> </u>	Natur	ral sunlight		
5 13.5 21 35.5e	12.11 16.92 25.98 30.05	9.62 19.60 13.82 13.19	71.79 48.80 44.67 36.61	0.40 0.43 5.05 7.81	87.97 85.76 89.53 87.66
		<u>Da</u>	rk Control		
24 48 120 168 264	1.75 2.11 4.09 6.29 11.00	0.00 0.00 0.53 4.11 9.79	90.02 91.61 87.39 85.39 77.01	1.77 2.13 2.84 0.47 1.59	93.65 95.84 94.85 96.25 99.35

a Figures represent an average of 3 replicates.

b [140]Radioactivity remaining in the soil hand.

c Oxypyrimidine is a degradate of diazinon.

d [14c]Radioactivity unidentified.

e The figures for 35.5 hours are an average of 2 replicates.

CASE GS0238 DIAZINON STUDY 3 PM --CHEM 057801 Diazinon BRANCH EAR DISC --FORMULATION OO - ACTIVE INGREDIENT FICHE/MASTER ID 00153229 CONTENT CAT 01 Martinson, J. 1985. Photolysis of diazinon on soil: Final Report Biospherics Project No. 85-E-044 SP. Unpublished study prepared by Biospherics Inc. 135 p. SUBST. CLASS = S. DUDSI. ULADS = 3. DIRECT RVW TIME = 5 (MH) START-DATE REVIEWED BY: J. Blake TITLE: Staff Scientist ORG: Dynamac Corp., Rockville, MD TEL: 468-2500 APPROVED BY: A. Abramovitch TITLE: Chemist ORG: EPA TEL: (703) 557-1392 SIGNATURE: DATE: MAR 28 1988

CONCLUSIONS:

Degradation - Photodegradation on Soil

- This sunlight photolysis data along with the data in Study 2 are acceptable 1. and satisfy EPA Data Requirement for photodegradation on soil.
- [14C]Diazinon (99% pure) degraded in sandy loam soil with a half-life of 2. 17.3 hours (14.7 days in the dark) when exposed to natural sunlight. The degradate, oxypyrimidine, was detected at maximum concentrations of 23.72% (32.6 hours) of applied after exposure to natural sunlight. The degradate 2-(1'-hydroxy-1'-methyl)ethyl-4-methyl-6-hydroxypyrimidine occurred only after 8 hours of natural light exposure at 3.6% but was not present in the dark control. An unidentified degradate accounted for about 7% of applied under sunlight as a result of non-photolytic degradation since it was also present in the non-exposed samples. The study provided a good account for the total material balance during the study.

MATERIALS AND METHODS:

A band (1 cm) of silica was removed from silica gel TLC plates (20 \times 20 cm) 2 cm from one end, and a slurry made from deionized water and sieved (250 mesh) California sandy loam soil (54.8% sand, 29.4% silt, 15.8% clay, 2.0% organic matter, 36.05% field capacity, CEC 15 meq/100 g, pH

24.5 microCi/mg, 99% pure, ClDa-Gelgy Colp., In ethyl alcohol ac an microgram aliquots were spotted on the the 1 cm soil band on the TLC plates. Some of the plates were placed 2 cm below four 4-foot Chroma 50 lamps (General Electric). Temperatures under the lamps ranged from 25 to 29°C. Samples were taken after 0, 1, 8, 24, 72, 168, 216, and 240 hours. Other plates were exposed to natural sunlight (Rockville, MD, latitude 39° Q2'N). The light intensities ranged from 15 to 300 footcandles/cm² (5-4600 microwatts/cm²) and the temperature ranged from 16 to 31°C during exposure. Samples were taken after 0, 1, 8, 21, 27.25, and 32.6 hours of exposure. Dark control plates were wrapped in aluminum foil and stored at 25+1°C.

The plates were developed with ethyl acetate:ethyl alcohol:ammonium hydroxide (90:5:5) in a saturated chamber and allowed to dry. The plates were viewed under UV light to detect visible spots, autoradiographed, and compared to standards. Radioactive zones were scraped from plates and analyzed by ISC. The soil from the plates was combusted and the resulting ω_2 was quantified by ISC.

REPURTED RESULTS:

[14C]Diazinon degraded in sandy loam soil on TLC plates exposed to natural sunlight with a half-life of 17.3 hours (Table 1). Degradation also occurred in the dark with about 63% of applied remaining after 240 hours (Table 2). The degradate, oxypyrimidine (see Appendix for structure), increased steadily with maximum concentrations occurring at 32.6 (23.72%), and 216 (17.40%) hours in the sunlight, and dark controls, respectively. The degradate, 2-(1'-hydroxy-1'-methyl)ethyl-4-methyl-6-hydroxypyrimidine, occurred only in the sunlight exposure after 8 hours. An unidentified degradate (3.6% of applied) was present in the sunlight exposed sample but not in the non-exposed sample. Bound [14C]radioactivity steadily increased with the maximum (about 30%) occurring in the sunlight exposure.

DISCUSSION:

- 1. The exposure of diazinon to sunlight data satisfied EPA data requirement. Photolytic degradation under sunlight was much faster (17.3 hours) than observed in non-exposed samples.
- 2. The artificial light did not simulate sunlight and the reported data under artificial light is of little significance in evaluating the environmental fate of diazinon. The chroma light spectra shown in the text does not indicate continuous radiation from 290 nm and above as provided by natural sunlight. Therefore, this portion of the study is unacceptable.

Table 1. Characteristics of <code>[14C]</code> radioactivity (% of applied) a from a band of sandy loam soil treated with <code>[14C]</code> diazinon at <code>-4.6</code> µg/µl on a TLC plate exposed to sunlight.

「14C]Radioactive	Sampling interval (hours)							
component	0	1	8	21	27.25	32.6h		
RoundC	1.45	2.15	10,55	20.65	21.00	30.11		
iazinon	96.85	93.20	63.70	35.30	35.95	25.51		
G-27550d	0.55	1.35	9.85	23.55	22.15			
S-31144e	க் த	´.e.	1.60	2.90	2.45	23.72		
known	••	••	6.90	9.35	9.25	2.43		
ckgroundf	2.15	2.21	5.50	5.80		7.09		
talg .	101.15	99.05	98.25	97.55	6.50 97.40	7.70 96.55		

a Figures represent the average of 2 replicates.

b Figures for 32.6 hours represent the average of 6 replicates.

c $\lceil 1^4 C \rceil$ Radioactivity residues remaining in the soil.

d G-27550 is oxypyrimidine (2-isopropyl-4-methyl-6-hydroxypyrimidine).

e GS=31144 is 2-(1'-hydroxy-1-methyl)ethyl-4-methyl-6-hydroxypyrimidine.

f Diffuse [14C]radioactivity, not associated with any compound.

⁹ Total % of applied [14C]radioactivity recovered.

Table 2. Characterization of [14C]radioactivity (% of applied)a from a hand of sandy loam soil treated with [14C]diazinon at ~4.6 $\mu g/\mu l$ on a TLC plate incubated in the dark at 25 \pm 1°C.

	Sampling interval (hours)									
[¹⁴ C]Radioactive component	0	1	8	24	72	168	216	240		
Roundb	1.45	1.35	1.70	1.85	2.65	4.95	4.75	4.35		
Diazinon	96.85	92.95	93.50	90.55	82.60	64.30	59.65	62.90		
G-27550¢	0.55	0.60	1.35	3.95	7.05	16.25	17,40	16.45		
GS-31144d	••	•.•	. .	••		••	•.•	••		
Unknown		••	0.75	••	5.90	11.70	15.50	13.50		
Rackgrounde	2.15	1.00	1.15	2.15	1.40	2.60	2.85	1.30		
Total ^f	101.15	95.90	98.45	99.60	99.65	99.85	99.95	99.35		

a Figures represent the average of 2 replicates.

b [14c]Radioactivity residues remaining in the soil.

c G-27550 is oxypyrimidine (2-isopropyl-4-methyl-6-hydroxypyrimidine).

d GS-31144 is 2-(1'-hydroxy-1'-methyl)ethyl-4-methyl-6-hydroxypyrimidine.

 $^{^\}circ$ e Diffuse $\lceil 140 \rceil$ radioactivity, not associated with any compound.

f Total % of applied [14 C]radioactivity recovered.

CASE GS0238 DIAZINON STUDY 4 CHEM 057801 Diazinon BRANCH EAB DISC --FORMULATION 00 - ACTIVE INGREDIENT FICHE/MASTER ID 00153231 CONTENT CAT 01 Martinson, J. 1985. Photodegradation of [carbon-14]-diazinon in water: Final Report: Biospherics Project No. 85-E-044 PW. Unpublished study prepared by Bio-CIRCT MACC - C SUBST. CLASS = S. DIRECT RVW TIME = 5 (MH) START-DATE REVIEWED BY: J. Blake TITLE: Staff Scientist ORG: Dynamac Corp., Rockville, MD TEL: 468-2500 APPROVED BY: A. Abramovitch TITLE: Chemist ORG: EPA TEL: (703) 557-1975 SIGNATURE:

CONCLUSIONS:

Degradation - Photodegradation in Water

- 1. This study is unacceptable because sunlight conditions were not simulated with the mercury vapor lamp.
- 2. [14C]Diazinon (87.7% pure) at 8.39 ppm in a buffered (pH 7) aqueous solution irradiated with a mercury vapor lamp, degraded, with a half-life of 55.9 hours. The degradate, oxypyrimidine, increased during irradiation to a maximum concentration of 35% of applied [14C]radioactivity at 150 hours. The amount of oxypyrimidine decreased to 16% after 362 hours (end of the experiment). Five unidentified degradates were present at a total of 59% of applied material.

MATERIALS AND METHODS:

Glass distilled, deionized water was buffered to about pH 7 with 0.067 M sodium dihydrogen phosphate and 0.67 M potassium phosphate. This aqueous solution was treated with radiolabeled (label position not specified) [14C]diazinon (specific activity 19.8 microCi/mg, 87.8% pure, Ciba-Geigy Corp.) at 8.39 ppm. One liter of the treated solution was placed in a glass photochemical reaction vessel and exposed to artificial light (450 watt UV mercury vapor lamp, Ace Hanovia Photochemical Lamp, No. 235322



DATE:MAR 28 983

out. The light intensity and temperature in the reaction vessels were 15,000-29,000 microwatts/cm² and 23.5-25.6°C, respectively, during the exposure period. A flask (70 ml) of the test solution was stoppered, covered with aluminum foil, and incubated at 25±1°C. Samples were taken at 0, 18, 42, 69, 100, 150, and 362 hours.

Duplicate aliquots (100 microgram) of the test solution were analyzed by LSC for total [14C]radioactivity. Duplicate aliquots (100 microliter) were also spotted on silica gel TLC plates and developed with toluene: chloroform:ethanol:formic acid (8:8:2:1) in a saturated chamber, dried, viewed under UV light, and autoradiographed. [14C]Radioactive zones were scraped and analyzed (in Maxifluor) by LSC. Comparison was made to standards.

REPORTED RESULTS:

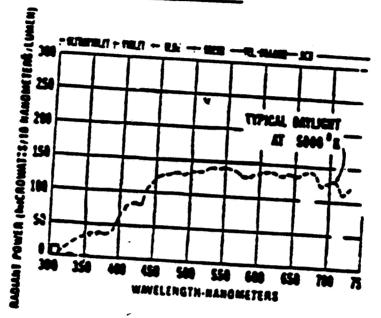
[14C]Diazinon at 8.39 ppm degraded in a buffered (pH 7) aqueous solution irradiated with a mercury vapor lamp with a half-life of 59 hours. The degradate, oxypyrimidine, increased during the irradiation period to a maximum concentration of 35% of applied [14C]radioactivity at 150 hours. The amount of oxypyrimidine decreased to 16% after 362 hours (the end of the experiment). Five unidentified degradates were present at 59% of the applied radioactive material.

DISCUSSION:

- 1. Sunlight conditions were not simulated. Radiation light below 290 nm was not filtered (according to the study report, filters of unspecified material were used to filter light below 280 nm but the actual spectra of the filtered light was not submitted), and as table I indicates the mercury lamp that was used did not provide continuous radiation above 290 nm as provided by natural sunlight
- 2. The test substance was reported to be analytical grade but was only 87.7% pure.



Natural Sunlight



Source: General Electric Corporation

Figure 1. Natural sunlight spectra for comparison with artificial light as presented in hardcopy.

Table 1. Spectral characteristics Canrad-Hanovia high intensity medium pressure mercury arc lamps operating at 200 watts per inch.

	Spectral line (Angstroms)	Watts/inch
Infrared	13673	0.9
	11287 10140	2.4 8.3
Visible	5780/90	14.0
	5461	15.4
	4358	12.2 6.1
	4045	. 0 - 1
Ultraviolet	3650/63	12.1
	3341	1.4
	3130	5.5 3.2
	3025	3.2
	2967	2.0
	2894	0.7 1.4
	2804	0.4
	275 <i>2</i> 2700	0.7
	2652	1.5
	2571	2.1
	2537	1.2
	2482	1.3
-	2400	1.2
Total		94.0 Watts/inch

lable 2. Characterization of $\lceil 14 \rceil \rceil$ radioactivity (% of recovered, TLC analysis) a from aqueous solution (pH 7) treated with $\lceil 14 \rceil \rceil$ diazinon at ~8.39 ppm and irradiated with a mercury vapor lamp or not irradiated.

[14c]Padioactive			Sampli	ng interva	1 (hours)		
component	0	18	42	69	100	150	362
			Irradia	ted			
Originb	. ••	0.15	0.60	1.05	0.65	3 60	.
Niazinon	91\55	90.85	88.85			7,00	22.8
G-27550c	2.75	3.75	8.05	15.60	66.40	40.70	1.70
Unknown #1		••			28.60	37.35	16.25
linknown #2			0.75	0.40	2.45	11.90	7.40
Unknown #3		1.0			0.45	5.10	••
Unknown #4	••	**	4		•		14.50
			:9.4		••	••	16.25
Unknown #5		••	••				10.60
Remaindere	5.65	4.35	1.75	1.50	1.40	1.30	
otal recovery	99.45	108.25	101.80	106.10	89.95		10.45
		D	ark contr		03.35	87.10	92.95
riginb	••		Conte				
iazinon	91.55	01 00		0.50	0.50	1.40f	1.85
-27550¢		91.30	93.55	97.40	95.40	88.00	86.15
emaindere	2.75	2.00	1.35	0.70	2.35	3.4	5.25
	5.65	6.70	5.10	1.40	2.25	7.3	6.70
tal recovery	99.45	114.4	86.85	106.15	97.90	110.6	87.55

a Figures represent the average of 2 replicates.

b [14C]Radioactivity remaining at the origin of the TLC plate.

c G-27550 is oxypyrimidine (2-isopropyl-4-methyl-6-hydroxypyrimidine).

d This figure represents the sum of Unknown #1 and #2.

 $^{^{\}rm e}$ It is assumed that this describes the diffuse [14C]radioactivity not associated with any compound.

f The figures for the dark control at 150 hours represent only one sample.

PM --STUDY 5 CASE GS0238 DIAZINON

CHEM 057801

Diazinon

BRANCH EAB

DISC --

FORMULATION 12 - EMULSIFIABLE CONCENTRATE (EC)

FICHE/MASTER ID 00011825 CONTENT CAT 01 Getzin, L.W., and I. Rosefield. 1966. Persistence of diazinon and zinophos in soils. J. Econ. Entomol. 59(3):512-516. Also In unpublished submission received May 12, 1972 under 100-501; submitted by Ciba-Geigy Corp., Greensboro,

NC: CDL:120412-E.

SUBST. CLASS = S.

DIRECT RVW TIME = 5 (MH) START-DATE

REVIEWED BY: J. Blake

TITLE: Staff Scientist

ORG: Dynamac Corp., Rockville, ✔D TEL: 468-2500

APPROVED BY: A. Abramovitch

TITLE: Chemist

ORG: EPA

TEL: (703) 557-1975

SIGNATURE: h

DATEMAR 28 SE3

CONCLUSIONS:

Metabolism - Aerobic Soil

- This portion of the study is scientifically acceptable but only provides 1. supplemental information because degradates were not identified and the soil moisture content was not maintained at 75% of 0.33 bar. However, EPA Data Requirements for Registering Pesticides for aerobic soil metabolism was satisfied with study 21 in combination with this study and study 7.
- 2. [14C]Diazinon (25% pure) at 5 g/cm² degraded in sandy losm, silt losm, silty clay loam and organic soils with half-lives of 2-4 weeks. [14C]-Radioactivity in the water-soluble and soil-bound fractions reached maximum concentrations in 1-4 weeks (20% of applied) and after 4 weeks (20-30% of applied), respectively.

Field Dissipation - Terrestrial

This portion of the study only provides supplemental information and 1. does not fulfill EPA Data Requirements for Registering Pesticides because the purity of the test substance was unspecified, pretreatment samples were not taken, degradates were not identified, complete field test data were not reported, and the material balance was insufficient.

 Diazinon (purity unspecified) at 5 lb ai/A dissipated from field plots of silt loam soil with a half-life of 4-8 weeks.

MATERIALS AND METHODS:

Metabolism - Aerobic Soil

Aliquots (300 cm³) of four moist, sieved (2mm), mineral soils and an organic muck (Table 1) were throughly mixed with ethoxy-labeled [14C]diazinon (specific activity 3.48 uCi/mg, 97% pure, Geigy Chemical Co.) made into an emulsifiable concentrate containing 70% xylene and 5% Triton X-100 for a final concentration of 5 ug/cm³. Water was added to the treated soils for a moisture level of 105% moisture equivalent, and the soil was placed in open, pint jars. The jars were set in a 2-gallon airtight chamber. Air (50-75 ml/minute) passed through a flask of 2 N sodium hydroxide for humidification and CO₂ removal, was drawn through the chamber, then through traps containing mineral oil or dimethyl sulfoxide, and then through traps containing 2 N sodium hydroxide (to trap volatile organics and CO₂, respectively). The soils were incubated at 25°C and triplicate samples (10 cm³) were taken at 0, 1, 2, 4, 8, 12, 16, and 20 weeks. The mineral oil or dimethyl sulfoxide and the sodium hydroxide traps were replaced weekly.

Soil samples were extracted 3 times with a mixture of 0.05 N calcium chloride (25 ml) and acetone (25 ml), centrifuged, and the extracts decanted. The acetone/water phase was extracted twice with chloroform, dried over anhydrous sodium sulfate, filtered, concentrated, and pipetted into planchets. Chloroform (0.2 ml) in shellac was added to the planchets, the solvent evaporated, and the residue analyzed by a gas-flow proportional counting detector. The chloroform/acetone fraction was also subjected to silica gel TLC using chloroform: acetone (9:1) and compared to standards. Subsequent [14C] radioactive spots were scraped from the plates and quantified by gas-flow detection. The aqueous phase from the original extraction was centrifuged and pipetted into planchets, allowed to dry (24-30 hours) and analyzed by gas-flow detection. The extracted soil was air-dried and subjected to gas-flow detection. The carbonate in the sodium hydroxide trap was precipitated as barium carbonate and washed with acetone. The barium carbonate, mineral oil, and dimethyl sulfoxide were analyzed for [14C] radioactivity by gas-flow detection. Recovery values for [14C]radioactivity from a silt loam soil fortified with diazinon at 5 ug/cm3 was 97+6%.

Field Dissipation - Terrestrial

Triplicate plots (35 x 20 feet) of Sultan silt loam soil (Table 1) were treated with diazinon (G, purity and source unspecified) at 5 lb ai/A which was immediately soil incorporated to a depth of 4-5 inches. The soil was compacted and seeded to corn. Soil samples (50 random cores, 6 inches deep, 1 inch diameter) were taken 0, 4, 8, 12, 16, and 24 weeks posttreatment. The samples were sieved (2 mm), mixed, and the moisture content was determined. Aliquots (42 g) were air-dired, Soxhlet extracted with redistilled acetone (1 hour), dried over anhydrous sodium sulfate, concentrated, and analyzed by GLC. Recovery values from soil fortified with diazinon at 1 ppm were 95+4%. The limit of detection was 0.1 ppm.

REPORTED RESULTS:

Metabolism - Aerobic Soil

 $\lceil 1^4 C \rceil$ Diazinon degraded in a sandy loam, silt loam, silty clay loam and organic soil with a half-life of $\sim 2\text{-}4$ weeks (Table 2, Figure 1). The $\lceil 1^4 C \rceil$ radioactivity in the water soluble fraction reached a maximum of < 20% of applied in 1-4 weeks; declining thereafter. The $\lceil 1^4 C \rceil$ radioactivity bound to the soil (unextractable) occurred at maximum concentrations of $\sim 20\text{--}30\%$ of applied after 4 weeks of incubation. Less than 1% of the $\lceil 1^4 C \rceil$ radioactivity was recovered in the mineral oil traps, and as much as $\sim 60\text{--}72\%$ of applied was not accounted for.

Field Dissipation - Terrestrial

Diazinon dissipated from field plots of silt loam soil with a half-life of 4-8 weeks. After 0, 4, 8, 12, 16, and 24 weeks diazinon was detected in the soil at 2.52 \pm 0.52, 1.32 \pm 0.17, 0.64 \pm 0.02, 0.40 \pm 0.05, 0.34 \pm 0.04, and 0.22 \pm 0.05 ppm, respectively. Soil temperatures ranged from 10 to 24°C during the experiment.

DISCUSSION:

Metabolism - Aerobic Soil

- 1. Although corrections were made for self-absorbance, as much as $\sim 72\%$ of the $\lceil 140 \rceil$ radioactivity was not accounted for; therefore, the material balance was insufficient.
- 2. Degradates were not identified.
- 3. The soil moisture content was maintained at 105% of the moisture equivalent and could not be related to 75% of 0.33 bar.
- 4. The Chehalis soil was reported to be a clay loam but according to the USDA soil classification system it is a silty clay loam.
- 5. The counting efficiency was not specified.

Field Dissipation - Terrestrial

- 1. The test substance was applied in the form of granules but its purity was unspecified.
- 2. Pretreatment samples were not taken.
- Degradates were not identified.
- 4. Complete field test data, such as the amount of rainfall or irrigation water, depth to the water table, slope of plots, and air temperature data were not reported.

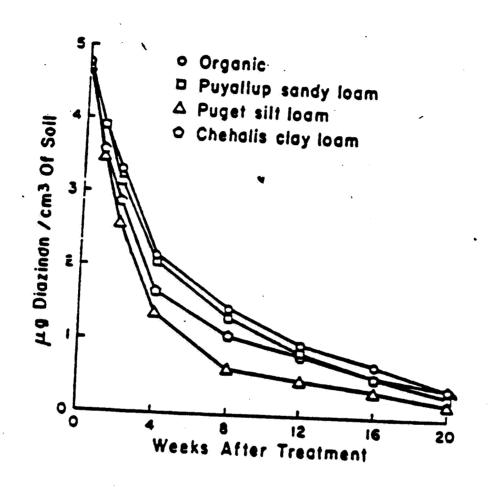


Figure 1. [14C]Diazinon (μ g/cm³) in four soils treated with [14C]-diazinon at 5 μ g/cm³ and incubated at 25°C, as presented in hardcopy.

Table 1. Soil characteristics.

Soil	Sand	Silt	Clay	Organic matter	CEC	Bulk density	Moisture equivalent	
type	·		.		(meq/100 g)	(g/cm ³)	(% of dry wt.)	þ
Puyallup sandy loam	54	38	8	2.1	7.7	1.3	8	5
Sultan silt loam	23	60	17	3.0	13.4	1.2	20	. 5
Puget silt loam	13	64	23	4.5	14.4	1.0	24	ŧ
Chehalis silty clay loam	17	47	36	7.2	32.8	1.0	34	5
Organic (muck)			•	40.0	49.1	0.6	79	Ę

zinon at 5 μ g/cm³ and incubated at 25°C.

Sampling interval (weeks)	Diazinona (Chloroform soluble)	Water soluhle	Soil bound	Unaccountableb
	Puy	allup sandy loam		
0 2 4 12 20	94 ± 4 63 ± 2 41 ± 1 17 ± 2 6 ± 1	1 8 7 3	6 ± 1 15 ± 1 25 ± 3 29 ± 3 31 ± 4	0 14 27 51 60
	<u>Pt</u>	get silt loam		
0 2 4 12 20	94 ± 3 51 ± 3 27 ± 4 9 ± 1 4 ± 1	1 20 19 3 2	5 ± 1 16 ± 2 28 ± 3 27 ± 1 26 ± 2	0 13 26 61 68
	Chehal	is silty clay lo	<u>am</u>	
0 2 4 12 20	96 ± 6 57 ± 6 33 ± 3 16 ± 1 8 ± 1	1 13 5 5 3	4 ± 1 17 ± 2 18 ± 1 19 ± 1 17 ± 4	0 13 44 60 72
	<u>(</u>	organic soil		
0 2 4 .2	95 ± 3 66 ± 2 43 ± 1 19 ± 1 8 ± 1	1 14 12 4 2	4 ± 1 14 ± 2 22 ± 2 29 ± 4 29 ± 1	0 6 23 48 61

a [14 C]Niazinon as determined by TLC and LSC of the chloroform soluble fraction.

b Percent unaccountable was calculated from the difference between the amount of radioactivity in the soil at the beginning of the experiment and the summation of the chloroform soluble, the water soluble, and the soil bound radioactivity at each sampling interval.

STUDY 6 CASE GS238 DIAZINON

CHEM 057801

Diazinon

BRANCH EAB

DISC --

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID 00095199 CONTENT CAT 01

Harris, C.R. 1969. Laboratory studies on the persistence of biological activity of some insecticides in soils. J. Econ. Entomol. 62(6):1437-1441. Also <u>In unpublished submission</u> received Aug. 28, 1972 under 3F1306; submitted by Dow Chemical Co., Indianapolis, IN; CDL:092219-G.

SUBST. CLASS = S.

DIRECT RVW TIME = 3 (MH) START-DATE

REVIEWED BY: J. Blake
TITLE: Staff Scientist

ORG: Dynamac Corp., Rockville MD

TEL: 468-2500

APPROVED BY: A. Abramovitch

TITLE: Chemist

ORG: EPA

TEL: 557-1975

SIGNATURE: Shamurit

DATEMAN 23 SEB

CONCLUSION:

Metabolism - Aerobic Soil

This study is unacceptable because the experimental procedures were inadequate to assess the degradation of diazinon in soil, a nonspecific bioassay was the only analytical procedure employed, the pattern of formation and decline of degradates was not addressed, and the soil moisture varied between 50 and 100% of field capacity.

MATERIALS AND METHODS:

Bulk quantities of loamy sand, (76.6% sand, 21.1% silt, 2.3% clay, 1.5% organic matter, pH 7.2) and a muck soil (14.5% sand, 38.8% silt, 46.7% clay, 64.6% organic matter, pH 6.5) were treated with diazinon (>95% pure, source unspecified) at 2.0 and 72.6 ppm, respectively. The treatment levels were equivalent to four times the application rate necessary to kill 50% of the first instar cricket nymphs, Acheta pennsylvanicus, placed in contact with the soil. The soils were mixed in an open container to distribute the pesticide and volatilize off

subsamples for each treated soil (500-g and 225-g moist subsamples of the loamy sand and muck soil, respectively). A single control the soil. A sample from each treated by mixing the carrier solvent into after treatment.

The loamy sand and muck soils were adjusted to 12.3 and 164.0% moisture, respectively, prior to bioassay. Three subsamples from each soil (50 g of sandy loam, 32 g of muck) were placed in cups with 10 first instar cricket nymphs along with food and water for the insects. Mortality counts were made after 20 hours. The assay was repeated the following day and the average mortality (corrected for natural mortality) of the six assays was used to estimate insecticidal activity.

The remaining samples were placed in sponge lined pots and incubated under continuous light at $80 \pm 1^{\circ}F$ ($26.7^{\circ}C$) and $65 \pm 5\%$ relative humidity. Distilled water was added to the samples on a weekly basis to maintain the moisture level between 50 and 100% of field capacity. Samples were bioassayed 1, 2, 4, 8, 12, 16, 24, 36, and 48 weeks after treatment. Sampling of the control samples was not reported.

REPORTED RESULTS:

Diazinon residues dissipated more rapidly in the loamy sand than in the muck soil. Mortality in the loamy sand decreased from 100% at day 0 to <5% at the end of 43 weeks. In the muck soil, mortality was >50% after 5 weeks, and decreased to <5% by 8 weeks.

DISCUSSION:

- The soil was incubated in a sponge lined pot. The sponge was used to absorb any excess water added to the soil. Losses of pesticide washed from the soil into the sponge were not considered in the study. Therefore, this study is scientifically invalid.
- A nonspecific bioassay was the only analysis used. Pesticide concentrations in the soils were not estimated from the assay and degradates were not determined.
- 3. The study was conducted over a 48-week period, but only a single control for each soil was included. Sampling procedures for the control were not reported, but if analysis was similar to that for the treated soils (analysis of entire sample) it may be assumed that the bioassay was performed at a single time interval. One control is not adequate to define background cricket mortality over a 48-week study.
- The soil moisture level was not held constant. It was reported to be 50-100% of field capacity, but the water was added apparently until the soil was more than saturated, with excess water being absorbed by the sponge. Therefore, the soil moisture was not quantitatively measured.

cording to the USDA soil textural classification system.

••••

CASE GS238 DIAZINON STUDY 7 CHEM 057801 Diazinon BRANCH EAB DISC --FORMULATION OO - ACTIVE INGREDIENT FICHE/MASTER ID 00073059 CONTENT CAT 01 Miles, J.R.W., C.M. Tu, and C.R. Harris. 1979. Persistence of eight organophosporus insecticides in sterile and nonsterile mineral and organic soils. Bull. Environ. Contam. Toxicol. 22:312-318. Also In unpublished submission received June 27, 1979 under 464-448; submitted by Dow Chemical U.S.A., Midland, MI: SUBST. CLASS = S. DIRECT RVW TIME = 3 (MH) START-DATE REVIEWED BY: J. Blake
TITLE: Staff Scientist ORG: Dynamac Corp., Rockville, MD TEL: 468-2500 -----APPROVED BY: A. Abramovitch

TITLE: Chemist ORG: EPA

TEL: 557-1975

SIGNATURE: Champrick DATE:

CONCLUSIONS:

Metabolism - Aerobic Soil

- 1. This study only provides supplemental information because a material balance was not provided, the purity of the test substance was unspecified, the patterns of formation and decline of degradation products were not addressed, and the soils were not completely characterized. However, EPA Data Requirements for Registering Pesticides for aerobic soil metabolism was satisfied with study 21. This study and study 5 provide supplemental information.
- 2. Diazinon (purity unspecified), at 10 ppm, degraded with a half-life of <1 week in nonsterile sandy loam soil and 2 weeks in nonsterile organic soil incubated in the dark at 28°C and 60% moisture holding capacity. There was 50% reduction in the concentration of diazinon in sterilized sandy loam and organic soil at 12.5 and 6.5 weeks, respectively.

MATERIALS AND METHODS:

Diazinon (analytical grade; purity and source unspecified) dissolved in pentane was applied at 10 ppm to 70-g aliquots of sieved (10-

-28-

mesh), sterile (autoclaved) and nonsterile sandy loam (2.9% organic matter, pH 8.0, 46% moisture holding capacity, soil not further characterized) and organic (48.7% organic matter, pH 7.6, 166% moisture holdling capacity, soil not further characterized) soils. Samples were maintained in the dark at 28°C and 60% of moisture holding capacity in hottles sealed with polyethylene film. Untreated sterile and nonsterile controls were also prepared. Soil samples were collected in triplicate at 0, 1, 2, 4, 8, 12, 16, 20, and 24 weeks post-treatment.

Soil samples were mixed with acetone for 15 minutes in an ultrasonic bath, then shaken with benzene:hexane (1:1) for 30 minutes. The supernatant was filtered through glass wool and extracted twice with distilled water to remove the acetone. The remaining benzene:hexane extract was dried with anhydrous sodium sulfate, and analyzed for diazinon by using GLC. The average recovery was 100%.

REPORTED RESULTS:

Diazinon degraded with a half-life of <1 week in nonsterile sandy loam and <2 weeks in nonsterile organic soil. Diazinon degraded with 95% breakdown in the nonsterile sandy loam and organic soils in 1 and 7 weeks, respectively— Degradation in sterilized soils was slower in both sandy loam and organic soil where 50% reduction in the concentration of diazinon was reached by 12.5 and 6.5 weeks, respectively.

Sterility in the sterilized soils was maintained through the 16th week of incuhation (<300 bacteria and <50 fungi/g soil), but most of the samples were not sterile by 24th week.

DISCUSSION:

- The formation and decline of diazinon degradates were not addressed.
- Complete soil characteristics, such at textural analysis and CEC, were not provided.
- A material balance was not provided.
- 4. The purity of the test substance was unspecified.
- The sterilization procedure, autoclaving 7 hours daily for 5 days, was extreme and may have altered soil physical-chemical characteristics that influence diazinon degradation. However, it is doubtful that the substantial differences in the rate of breakdown between sterile and nonsterile soil resulted from changes in the chemical reactivity of the sterilized soil.

CASE GS238 DIAZINON STUDY 8 PM --CHEM 057801 Diazinon

BRANCH EAB

DISC --

FORMULATION 04 - GRANULAR (G)

FICHE/MASTER ID 00092604 CONTENT CAT 01

Rusk, H.W., S. Esvelt, and B.J. Landis. 1965. Report of residue analysis: Report No. PCY-65-30. U.S. Agricultural Research Service, Entomology Research Div., Pesticide Chemicals Research Branch, Potato, Pea and Sugar Beet Insects Investigations; unpublished study; CDL:091231-B.

SUBST. CLASS = S.

DIRECT RVW TIME = 2 (MH) START-DATE

REVIEWED BY: J. Blake

TITLE: Staff Scientist

ORG: Dynamac Corp., Rockviller MD

TEL: 468-2500

APPROVED BY: A. Abramovitch

TITLE: Chemist ORG: EPA TEL: 557-1975

SIGNATURE:

DATE: MAR 28 1563

CONCLUSION:

Field Dissipation - Terrestrial

This study is unacceptable because the analytical method was not described in sufficient detail to properly assess the dissipation of the test substance from soil. In addition, this study would not fulfill EPA Data Requirements for Registering Pesticides because the test soil was not completely characterized, meteorological data were not provided, residues were not identified, dissipation of diazinon in soil confined in 55-gallon drums may not be representative of dissipation under actual field conditions, and vertical movement of residues was not addressed.

MATERIALS AND METHODS:

Soil containers, prepared by cutting 55-gallon drums in half and removing both ends, were filled with a layer of gravel and 6 inches of untreated Sagemoor loam soil (soil not further characterized). Soil samples were treated with diazinon (5% G, source unspecified) at 2 lb ai/A and layered over the untreated soil to a total depth of 14 inches. The containers were located outdoors (near Yakima, Washington) and watered twice weekly

(2 gal/week) to compensate for evaporative losses. Soil cores, (6 inches deep and 1-inch in diameter) taken immediately posttreatment and at approximately 2-week intervals, were frozen until analysis (5-7 months).

Each sample was mixed and a subsample was bioassayed using wireworms. If toxic, the remaining sample was analyzed for residues. Samples were air-dried to 3-5% moisture, extracted with chloroform, and filtered through sodium sulfate. The filtrate was placed into porcelain crucibles with chloroform and bromine water (1 ml) and held at room temperature for 30 minutes. A carborundum chip was added and the samples were analyzed by a referenced (not provided) procedure (Saliman. 1964. A new digestion reagent for the determination of microgram quantities of phosphorus in organic compounds. Anal. Chem. (36) 112). Recovery values for diazinon in soil fortified with diazinon at 0.2 and 1.0 ppm were 71.6 and 108.8%, respectively. The limit of sensitivity was 0.08 ppm.

REPORTED RESULTS:

Diazinon in control samples was <0.08 ppm. Diazinon residues in loam soil dissipated with a half-life of \sim 28-42 days with an average of 1.7, 1.4, 0.89, 0.75, and 0.40 ppm detected in the soil on days 0, 14, 28, 42, and 56, respectively.

- The analytical method was not described in sufficient detail to properly assess the dissipation of diazinon from soil.
- Complete soil characteristics, such at textural analysis, pH, organic matter content, and CEC, were not reported.
- 3. Meteorological data (rainfall, soil temperature) were not reported.
- 4. Diazinon residues were not identified or quantified.
- 5. The soil was maintained in 55-gallon drums; dissipation of diazinon under these conditions may not be representative of dissipation under actual use conditions.

CASE GS238 DIAZINON STUDY 9 PM --CHEM 057801 Diazinon BRANCH EAB DISC --FORMULATION 12 - EMULSIFIABLE CONCENTRATE (EC) FICHE/MASTER ID 00053135 CONTENT CAT 01 Ciba-Geigy Corporation. 1974. The influence of soil humidity, amount and intensity of rainfall on the leaching behavior of pesticides: No. SPR 44/74. Unpublished study received Oct. 8, 1976 under 7G1877; CDL:095322-G. SUBST. CLASS = S. DIRECT RVW TIME = 2 (MH) START-DATE REVIEWED BY: J. Blake TITLE: Staff Scientist ORG: Dynamac Corp., Rockville, MD TEL: 468-2500 APPROVED BY: A. Abramovitch TITLE: Chemist ORG: EPA TEL: 557-1975 DATE: MAR 28 983 SIGNATURE:

CONCLUSION:

Mobility - Leaching and Adsorption/Desorption

This study is unacceptable and would not fulfill EPA Data Requirements for Registering Pesticides because the test substance was not technical grade or purer, K_d values were not provided, the soil columns were leached with an insufficient amount of water (7.87 inches) and the analytical method was not described.

MATERIALS AND METHODS:

Diazinon (Basudin 25% EC, source unspecified) at 5 lb ai/A (630 ug) was applied to 30 cm columns of either air-dried or prewetted soils (Table 1). The columns were leached with 20 cm (7.87 inches) of water over a 48 hour period. The leachate and the soil columns (2 cm segments) were analyzed by an undescribed method.

REPORTED RESULTS:

Diazinon was slightly mobile in the soils tested; no leaching occurred below 8 cm in any of the soil columns (Table 2).

Gall

DISCUSSION:

- 1. The analytical methods were not described; therefore, proper assessment of diazinon mobility in soil was not possible.
- 2. The test substance was not technical grade or purer.
- The columns were leached with an insufficient amount of water (7.87 inches).
- 4. Soil/water relationship (K_d) values were not provided.

Edl

Table 1. Soil characteristics.

Origin	Soil type	Sand	Silt	Clay	Organic matter	CaCO3	рН
Switzerland	Collombey sand	87.0	10.2	2.8	2.2	11.5	7.8
Switzerland	Les Evouettes loam	38.4	49,4	12.2	3.6	0	6.1
Switzerland	Vetroz sandy clay loam	57.8	19.6	22 . 6	5,6	15.0	6.7

Poll

Table 2. Diazinon residues (% recovered) in columns of three soils treated with diazinon at ~5 lb ai/A and leached with 20 cm of water.

Sampling depth (cm)	·	Soil typ	<u>e</u>
(cm)	Sand	Loam	Sandy clay loam
	<u> </u>	ir-dried soil	
0-2	19.5	78.1	92.7
2-4	34.1	14.9	<0.5a
4-6	25.5	<0.5	<0.5
6-8	2.0	~<0.5	<0.5
8-30b	<0.5	<0.5	<0.5
ater phase	<0.5	<0.5	<0.5
otal C recovered)	81.1	93.1	92.7
	, <u>P</u>	rewetted soil	
-2	10.9	70.9	72.7
-4	23.6	10.0	<0.5
l - 6	32.7	<0.5	<0.5
i - 8	15.5	<0.5	<0.5
-30b	<0.5	<0.5	<0.5
ter phase	<0.5	<0.5	<0.5
tal recovered)	82.7	80.9	72.7

a The detection limit was not specified.

h Analyzed in 2 cm-segments; <0.5% recovered in any segment.

CASE GS0238 DIAZINON STUDIES 22 PM -CHEM 057801 Diazinon BRANCH EAB DISC -ACTIVE INCREDIENT-ring radiolabelled diazinon with a specific activity of 2.79 uCi/mg and 99% purity. FICHE/MASTER ID 00132735 Buckhard, N., T. Winkler, and K. Ramsteiner. 1980. Leaching characteristics of aged 14C-diazinon (Basudin) residues in two standard soils: Project Report 09/80. Unpublished study received Nov. 17, 1983 under 100-469; prepared by Ciba-Geigy Ltd., Switz., submitted by Ciba-Geigy Corp., Greensboro, NC; CDL:251777-P. FICHE/MASTER ID 00132734 Buckhard, N., T. Winkler, and K. Ramsteiner. 1979. Leaching characteristics of aged ¹⁴C-diazinon (Basudin) residues in two standard soils: Project Report 42/79. Unpublished study received Nov. 17, 1983 under 100-469; prepared by Ciba-Geigy Ltd., Switz., submitted by Ciba-Geigy Corp., Greensboro, NC; CDL:251777-0. SUBST. CLASS = S. DIRECT RVW TIME = 5 (MH) START-DATE END DATE REVIEWED BY: A. Abramovitch TITLE: Chemist ORG: US EPA TEL: 557-1975 APPROVED BY: P. Mastradone TITLE: Acting Chief ORG: US EPA TEL: (703) 557-7347 Paul Mastradone SIGNATURE:

CONCLUSIONS:

Mobility-Aged Leaching:

- 1. MRID 00132734 and 00132735 are identical submissions. The studies listed above provide supplemental information since the extent of leaching cannot be adequately assessed with 20.3 cm of simulated rainfall instead of the required 50 cm. These studies were also evaluated in the EAB reviews of May 8, 1984 and Dec. 5, 1986 (EAB# 5794 & 4080). This studies alone do not satisfy EPA Data Requirement for Registering Pesticides.
- 2. Aged residues of diazinon were observed in the leachate of a 30 cm sandy soil column of pH 7.8 when leached with 20.3 cm of water. Oxypyrimidine was the major degradate found in the leachate.

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DATE: MAR 28 1989

MATERIALS AND METHODS:

The soil characteristics of the soils used in the aged leaching study were as follows:

Soil	pН	%OM	% Silt	% Clay	% Sand
Collombey	7.8	2.2	2.8	10.2	87
Les Evouettes	6.1	3.6	12.2	49.4	3 8.4

Soil columns (40 cm length, 4 cm in diameter) were filled to a height of 28 cm with each soil. Then at the top of each column was added, 2 cm of the corresponding soil that was treated at a level of 4 lb ai/acre and aged for 30 days at 25°C. Each column was irrigated for 16 days for a total of 20.3 cm of rainfall. The amount of radioactive residues was determined by LSC and their identity by TLC and GLC. Degradates were also isolated and their identity established by GLC/MS and NMR. For the purpose of GLC analysis, residues were methylated with diazomethane.

REPORTED RESULTS:

Addition of 20.3 cm of simulated rainfall within 16 days to each soil column resulthed in 21.3 and 4.0% leaching of the applied radioactivity of 30 days aged radiolabeled diazinon from 30 cm Collombey and Les Evouettes Swiss soils, respectively. Greater than 75% of the ¹⁴C material in the leachate was extracted into methylene chloride. Oxypyrimidine was identified in the leachte. Another degradate was tentatively identified as 2-ethyl-4-methyl-6-hydroxypyrimidine.

- 1. The study was conducted with 20.3 cm of water instead of the required 50 cm.
- 2. The study was conducted on foreign soils that were fully characterized.
- 3. The soils were not analyzed to determine the vertical movement of diazinon and its degradates. However, the presence of degradates in the leachte indicated that oxypyrimidine and related compounds can leach.



CASE GS0238

DIAZINON

STUDIES 23

PM ---

CHEM 057801

Diaziron

BRANCH EAB

DISC -

ACTIVE INCREDIENT-ring radiolabelled diazinon with a specific activity of 2.79 uCi/mg and 99% purity.

FICHE/MASTER ID 00118034

Buckhard, N. 1980. Leaching characteristics of aged 14C-diazinon (Basudin) residues in two standard soils: Project Report 09/80. Unpublished study received Nov. 5, 1982 under 4581-351; prepared by Ciba-Geigy Ltd., Switz., submitted by Agchem Div., Pennwalt Corp., Philadelphia, PA; CDL: 248818-0.

SUBST. CLASS = S.

DIRECT RVW TIME = 5 (MH) START-DATE

END DATE

REVIEWED BY: A. Abramovitch

TITLE: Chemist ORG: US EPA TEL: 557-1975

APPROVED BY: P. Mastradone

TITLE: Acting Chief

CRG: US EPA

(703) 557-7347 TEL:

SIGNATURE:

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CONCLUSIONS:

Mobility-Aged Leaching:

This study provides supplemental information. The study was also evaluated 1. in the EAB reviews of May 8, 1984 and Dec. 5, 1986 (EAB# 5794 & 4080).

This study cannot satisfy EAB data requirement for aged leaching until the identity of the second major component in the leachate is fully identified (see Discussion). With complete identification of the leachate, the data requirement for aged leaching data will be satisfied. The unaged soil leaching data requirement was satisfied by study 25.

Aged residues of diazinon were observed in the leachate of a 30 cm sandy 2. soil column of pH 7.8 when leached with 50.7 cm of water. About 32.7% of the applied material leached through the Collombey sand soil column and 25.3% through the sandy loam soil column. Most of the leached material leached through with the initial application of less than 30 cm of irrigation. Oxypyrimidine, the primary degradate, was found in the leachate along with another degradate whose identity was not fully established.

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Dried soil samples of Collombey sand and Les Evouettes-loam were treated with ring labeled ¹⁴C-diazinon in methylene chloride at 12.6 and 18.9 ppm, respectively. The fortification level was equivalent to a 2 cm layer at 4.0 lb ai/acre. The soil characteristics of the study were as follows:

Soil	pH	MOS	% Silt	% Clay	% Sand
Collambey		2.2		10.2	87
Les Evouettes	6.1	3.6	12.2	49.4	38.4

The soils were wetted with distilled water to 50% of the moisture holding capacity and incubated at 25°C in the dark for 30 days. Water saturated air flow kept the moisture content constant and volatiles including $^{14}\rm CO_2$ were trapped with ethylene glycoI monomethyl ether, NaOH and sulfuric acid traps.

Soil columns (40 cm length, 4 cm in diameter) were filled to a height of 28 cm with each soil. Then at the top of each column was added, 2 cm of the corresponding 30 day aged soil. Each column was irrigated with 1.27 ml of water for 45 days for a total of 57.3 cm equivalent of rainfall. The amount of radioactive residues in the leachate was determined by ISC and their identity by TIC and GLC. Degradates were also isolated and their identity established by GLC/MS and NMR. For the purpose of GLC analysis, residues were methylated with diazomethane. The soil columns were fragmented into 2 cm sections, extracted in a soxhlet apparatus with acetone and then with methanol and the extract was analyzed by ISC to determine the amount of extractable soil residues. Dried soils analyzed by combustion to quantify the amount of unextracted 14C residues.

REPORTED RESULTS:

After 30 days of aerobic aging, 96.1 and 89.4% of the applied radioactivity to the Collombey sand and Les Evouettes loam Swiss soils, respectively. Irrigation of these columns with 57.3 cm of water indicated that with time aged soil residues leached through both columns. The major component of the leachate was a degradate whose identity was not established (see discussion). A second major component was the primary degradate 2-isopropyl-4-methyl-6-hydroxypyrimidine (oxypyrimidine). Greater than 75% of the 14C material in the leachate was extracted into methylene chloride. Oxypyrimidine was identified in the leachate. Another degradate was only tentatively identified (see Discussion).

- In addition to the primary degradate, exypyrimidine another major degradate was reported in both the aerobic soil metabolism data and the aged columns leachate. The aerobic soil data reported 2-(1'-hydroxy-l'-methyl)ethyl-4-methyl-6-hydroxypyrimidine as a secondary degradate. The aged soil column leaching only identified 2-ethyl-4-methyl-6-hydroxypyrimidine as a secondary component in the leachate. The identification of the latter compound in the leachate appear to be questionable. This discrepancy should be ressolved by the registrant.
- The study was conducted on foreign soils that were fully characterized.

Simulated	14C is	14C in eluate (% of applied)				
rainfall (in.)	Collombey sand	Les Evouettes loan				
3.0-3.5	<0.1ª	<0.1ª				
3.5-4.0	<0.1	<0.1				
4.0-4.5	0.51	<0.1				
4.5-5.0	2.23	<0.1				
5.0-5.5	3.85	<0.1				
5.5-6.0	5.12	0.15				
6.0-6.5	3.89	0.45				
6.5-7.0	2.34	1.07				
7.0-7.5	2.08	1.83				
7.5-8.0	1.43	1.61				
8.0-8.5	1.60	3.21				
8.5-9.0	1.34	2.76				
9.0-9.5	1.14	2.35				
9.5-10.0	1.04	1.88				
10.0-1.05	0.75	1.35				
10.5-11.0	0.74	1.20				
11.0-11.5	0.63	1.07				
11.5-12.0	0.59	1.03				
12.0-12.5	0.93	0.40				
12.5-13.0	0.17	. 0.62				
13.0-13.5	0.35	0.81				
13.5-14.0	0.21	0.72				
14.0-14.5	0.19	0.70				
14.5-15.0	0.15	0.75				
15.0-15.5	0.45	<0.1				
15.5-16.0	0.12	0.48				
16.0-16.5						
16.5-17.0	0.12	0.44				
17.0-17.5	0.12	0.37				
	0.11	0.31				
17.5-18.0	<0.1 ^b	0.14				
18.0-18.5	<0.1	0.18				
18.5-19.0	<0.1	0.16				
19.0-19.5	<0.1	0.28				
19.5-20.0	<0.1	<0.1 ^b				
20.0-20.5	<0.1	<0.1				

a No radioactivity (<0.1%) was detected in the leachate in the first 0-3.0 inches of simulated rainfall.</p>

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b No radioactivity (<0.1%) was detected in subsequent leachate.

Distribution of $^{14}\mathrm{C}$ in the eluate from leaching aged [$^{14}\mathrm{C}$]diazinon treated soil.

	14C Distribution (% of applied)							
Soil	IMHba	Ab .	Unidentified -	Total				
Collombey Les Evouettes	9.8 7.8	15.2 13.4	7.7 4.1	32.7 25.3				

a 2-Isopropyl-4-methyl-6-hydroxypyrimidine. b 2-Ethyl-4-methyl-6-hydroxypyrimidine.

Distribution of extractable and nonextractable $^{14}\mathrm{C}$ in columns of aged [$^{14}\mathrm{C}$]diazinon treated soils after leaching with 57.3 cm of artificial rainfall.

Depth in. column (cm)	San	dy soil (Collombey)	Silty loam (Les Evouettes)				
	Acetone	Methanol	Residual	Totala	Acetone	Methanol	Residual	Total	
0 - 2	5.5	0.3	8.3	14.1	2.9	0.3	7.4	10.6	
2 - 4	2.3	0.2	4.1	6.6	5.3	0.6	8.5	14.4	
4 - 6	2.0	0.2	2.7	4.9	6.2	0.8		12.4	
6 - 8	2.0	<0.1	2.1	4.1	5.0	0.7	2.5	8.2	
8 - 10	1.2	<0.1	0.7	1.9	1.7	0.3	0.9	2.9	
10 - 12	0.4	<0.1	0.3	0.7	0.3	<0.1	0.6	0.9	
12 - 14	<0.1	<0.1	0.1	0.1	0.1	<0.1	0.4	0.5	
14 - 16	<0.1	<0.1	0.1	0.1	0.1	<0.1	0.3	0.4	
16 - 18	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.3	0.3	
18 - 20	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.3	0.3	
20 - 22	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.2	0.2	
22 - 24	<0.1	<0.1	<0.1	<0.1	₹0.1	<0.1	0.1	0.1	
24 - 26	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	
25 - 28	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	
28 - 30	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	

a $14\mathrm{C}$ not extracted by acetone and methanol.

(TDRO3B) DATA EVALUATION RECORD PAGE 1 OF CASE GS0238 DIAZINON STUDIES 24 CHEM 057801 Diazinon BRANCH EAB DISC --ACTIVE INGREDIENT-analytical grade ring radiolabelled diazinon. FICHE/MASTER ID 00118032 Guth, J., and R. Imhof. 1972. Adsorption and leaching behaviour of diazinon in various soils: SPR 46/72 S. Unpublished study received Nov. 5, 1982 under 4581-351; prepared by Ciba-Geigy Ltd., Switz., submitted by Agchem Div., Pennwalt Corp., Philadelphia, PA; CDL:248818-M. (00118032) SUBST. CLASS = S. DIRECT RVW TIME = 5 (MH) START-DATE END DATE REVIEWED BY: A. Abramovitch TITLE: Chemist ORG: US EPA TEL: 557-1975

APPROVED BY: P. Mastradone TITLE: Acting Chief

ORG: US EPA

TEL: (703) 557-7347

SIGNATURE: Paul Mastaslone

DATE:

CONCLUSIONS:

Mobility-Adsorption/Desorption:

- 1. This study should provide supplemental information provided satisfactory answers are given to questions raised in the Discussion section. The study was also evaluated in the EAB reviews of May 8, 1984 and Dec. 5, 1986 (EAB# 5794 & 4080). This study cannot satisfy EAB data requirement for unaged leaching until the answers to questions raised in the Discussion are evaluated. Satisfactory response should render the reported Kd values acceptablle.
- Provided satisfactory answers are provided to render the study acceptable, the reported Kd values for diazinon in the range of 3.7 to 5.6 in three sandy soils containing between 82-91% sand and 1-2.2% organic matter, would indicate moderate mobility for diazinon. That would also support the registrant's claim that diazinon is less likely to leach than its degradates. The Kd values were directly proportional to the organic material content.

MATERIALS AND METHODS:

Analytical grade radiolabeled diazinon was used to prepare stock solutions of 0.5, 1.0, 2.5, 5.0 and 10.0 ppm. The soil characteristics of the study were as follows:

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Table 1

Crimin and properties of Swiss soils used for adsorption reasurements

Crigin'	НФ	Ca CO.,	Organic	Kechanical Analysis			
	% % %			Clay S	Silt #	Sani s	
Collombey VS	7.8	11.5	2.2	2.8	10.2	د.73	
Illarsaz VS	7.5	6.0	22.9	•	*	*	
Les Evouettes VS	6.1	0 •	3.6	12.2	49.4	<i>3</i> 8.4	
Uvrier I VS	7.4	8.5	1.0	3.4	5.0	91.5	
Uvrier II VS	8.1	12.0	1.6	4.1	13.8	82.1	
Vetroz VS	6.7	15.0	5.6	22.6	19.6	57.9	

Five 50 gm oven-dried soils were mixed with the five 100 ml aliquots of the stock solutions. The soil suspensions were shaken for 24 hours at 20°C. The liquid was then separated from the soil by centrifuging at 5000 rev/min for 20 minutes. Aliquots of 0.5 ml were taken and assayed by LSC. The amount of radiolabeled material adsorbed to the soil was determined by subtracting the initial water concentration from the concentration at equilibrium and were not confirmed by combustion analysis. The results were assessed with the aid of the Freundlich adsorption isoterm.

 $\log X/M = \log k + 1/n \log Ce$

Where X/M is the amount adsorbed by unit mass by soil/water, Ce is the initial concentration in water and n and k are contants.

The reported values of k are obtained for Ce of 1

M

Table 2

Constants from Freundlich adsorption isotherms for discinon with various

Swiss soils

Soil	k pg/g soil	k * µg/g organic matter	<u>1</u>
Collembey	5.6	255	0.63
Illarsaz	113.5	496	0.70
Les Evouettes	22.7	3 25	0.77
Uvrier I	3.7	370	0.60
Uvrier II	4.5	281	0.55
Vetroz	23.4	418	0.93

DISCUSSION:

- 1. The study appears to provide acceptable data that can be used in fullfillment of the unaged soil leaching data requirement provided that the registrant provides the following information:
 - 1) Stability data on diazinon under the equilibrium condition.
 - 2) Whether 50 gm soil samples were used in each case (in the text 5 to 50 gm of oven-dry soil. Should it be five 50 gm soil samples since five concentrations were used?)
 - 3) The purity of the "analytical sample"
 - 4) combustion data on the soil samples if available.
 - 5) Comparison to US soils.
- 2. The study was conducted on foreign soils that were fully characterized but were not compared to US soils.

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^{*} Due to the high organic matter content, texture analysis was not possible.

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Fie.	2 Linear relationship between Freundlich
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CASE GS238 DIAZINON STUDY 10 PM --CHEM 057801 Diazinon BRANCH EAB DISC --FORMULATION 01 - TECHNICAL CHEMICAL (TECH) FICHE/MASTER ID 00122690 CONTENT CAT 01 Harris, C. 1969. Movement of pesticide in soil. J. Agr. Food Chem. 17(1). Also In unpublished submission received Nov. 19, 1982 under HI 79/2; submitted by Velsicol Chemical Corp., Chicago, IL; CDL:248932-D. SUBST. CLASS = S. DIRECT RVW TIME = 4 (MH) START-DATE END DATE REVIEWED BY: J. Blake TITLE: Staff Scientist ORG: Dynamac Corp., Rockville, MD TEL: 468-2500 APPROVED RY: A. Abramovitch TITLE: Chemist ORG: EPA TEL: 557-1975

CONCLUSIONS:

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Mobility - Leaching and Adsorption/Desorption

- This study is unacceptable and does not fulfill EPA Data Requirements for Registering Pesticides because subirrigated soil columns studies do not provide downward mobility data as required. Also, the purity of the test substance was not reported, the test soils were not completely characterized, the amount of water absorbed by the column was not reported, and Kd values were not calculated.
- 2. Diazinon (TECH, purity unspecified) was slightly mobile in both Hagerstown silty clay loam and Lakeland sandy loam soils, based on upward movement in subirrigated soil columns.

MATERIALS AND METHODS:

Diazinon (TECH, purity and source unspecified) at 20 lb/A in ethanol was applied to the top of a 4.4 cm packing of air-dried Hagerstown silty clay loam soil (30% clay, 4.3% organic matter, CEC 12.5 meq/100 g, pH 5.5) and Lakeland sandy loam soil (10% clay, 3.3% organic matter, CEC 2.9 meq/100 g, pH 6.2) in duplicate aluminum columns (7.6 cm i.d.) for each soil. After

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respective air-dried soils to a total depth of 17.8 cm and soil bulk densities of 1.2 and 1.4 g/cc. The columns were subirrigated with water at 2.5 cm head for 3 days, then sliced into 1.0 inch segments. Each segment of soil was seived (2 mm) and mixed.

Subsamples (15 g) of each segment were shaken with hexane:2-propanol (3:1), decanted, then rinsed twice with additional solvent. The extract and rinses were combined, filtered, washed three times with equal volumes of water, then dried over anhydrous sodium sulfate. The extract was diluted to analytical volume, analyzed by a GC equipped with an electron-capture detector operating in the halidespecific mode and quantified by peak height comparison to standards.

Mobility factors were calculated by normalizing the mg of test substance recovered per column segment so that the sum of the values from all column segments equaled 1.0, weighting (multiplying) the normalized values inversely according to segment depth, then totaling the weighted values. The mobility factor scale ranged from 1.0 for no movement from the treated segment to 6.0 for maximum movement.

REPORTED RESULTS:

Diazinon was slightly upwardly mobile with calculated upwardly mobility factors of 1.6 and 1.4 in the silty clay loam and sandy loam soils, respectively (Table 1). The total recovery of diazinon in Hagerstown silty clay loam and Lakeland sandy loam soil columns was 39 and 82% of the applied, respectively.

- 1. The experimental method did not provide information about the <u>downward</u> mobility of diazinon in soils, since it only tested the <u>upward mobility</u>. Also, the amount of water absorbed by soil columns was not reported.
- 1. The purity of the test substance was not specified.
- 2. Complete soil characteristics, such as complete textural analysis, were not provided.
- 4. The analytical recovery values, fortification levels, and limit of detection for the GC method were not provided.
- 5. Soil/water relationship values (Kd) were not reported.

Table 1. Diazinon (mg) in layers of silty clay loam and sandy loam soils treated with diazinon at 20 lb/A and subirrigated in columns.

Soil	Sampling depth (inches)								
type	. 0-1	1-2	2-3	3-4	4-5	5-6	Total (mg)	Total (% of applied)	Mobilit factor
Hagerstown silty clay loam	0.00	0.00	0.00	0.22	2.04	1.28	4.04	39	1.6
Lakeland sandy loam	0.00	0.00	0.00	0.46	2.99	5.04	8.46	82	1.4

a The mobility factor scale was 1.0 for no movement from the treated segment to 6.0 for maximum movement.

CASE GS0238 DIAZINON STUDY 11 PM --CHEM 057801 Diazinon BRANCH EAB DISC --FORMULATION 09 - MICROENCAPSULATED (MCAP), 12 - EMULSIFIABLE CONCENTRATE (EC) FICHE/MASTER ID 00118022 CONTENT CAT 01 Agchem. 1979. Knox Out 2FM and diazinon E.C .-- soil leaching: Project No. WI-2-78. Unpublished study received Nov. 5, 1982 under 4581-351; CDL:248818-C. SUBST. CLASS = S. DIRECT RVW TIME = 2.5 (MH) START-DATE REVIEWED BY: J. Blake TITLE: Staff Scientist
ORG: Dynamac Corp., Rockville, MD TEL: 468-2500 APPROVED BY: A. Abramovitch TITLE: Chemist ORG: EPA TEL: 557-1975 SIGNATURE: DATEMAP 23 SES

CONCLUSION:

Mobility - Leaching and Adsorption/Desorption

This study is unacceptable because the analytical method was not described in sufficient detail to adequately assess the mobility of the test substance in soil. In addition, the columns were leached with an insufficient volume of water (15.7 instead of 20 inches) and the test substance was not technical grade or purer.

MATERIALS AND METHODS:

Glass soil columns (50 x 4 cm, length x diameter) were filled to a depth of 30 cm with each of four soils (Table 1) and treated with 1 ml of diazinon (Knox Out 2FM, 23% or 2 lb ai/gal MCAP, or EC, purity unspecified, source unspecified) at 605 ug ai/ml (EC) or 670 ug ai/ml (MCAP) in water. The columns were leached with 500 ml (15.7 inches) of water. The leachate was collected, and the soil columns were sectioned in 10 cm segments. Soil and water were solvent extracted and analyzed for diazinon using a GLC equipped with a flame photometric detector (analytical method not further described).

soils were treated with 1 ml of diazinon (Knox Out 2FM, 23% or 2 lb ai/gal MCAP, source unspecified) at 690 µg ai/ml in water and leached with 500 ml of water. The top 4 cm of each soil column was sectioned into 2 cm portions and the soil was analyzed as above.

REPORTED RESULTS:

The EC formulation of diazinon was mobile in sand leaching to the 20-30 cm soil segment in the column, and less mobile in the sandy loam, the silty clay loam and the silt loam soils (Table 2). The MCAP formulation was less mobile with >88% of applied detected in the top 2 cm of the soil.

DISCUSSION:

- 1. The analytical method was described in insufficient detail to adequately assess the mobility of diazinon in soil.
- The test substance was not technical grade or purer.
- 3. The columns were leached with an insufficient volume of water (~15.7 inches).
- Soil/water relationship (K_d) values were not reported.

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Table 1. Soil characteristics.

Soil type	Sand	Silt	Clay	Organic matter	CEC (meq/100 g)	рн
Lakeland sand	93	3	4	<1.0	2.0	4.5-5.0
Alderwood sandy loam	71	23	6	5.6	18.8	4.55
Woodburn silty clay loam	7	55	38	2.6	15.0	5.3
Sultan silt loam	25	57	18	2.9	15.9	5.4

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the supernatant was decanted. The soil samples were extracted with acetonitrile and the solutions were filtered. The supernatant samples were analyzed for diazinon by the AOAC method for organophosphate pesticides using a phosphorus specific detector.

REPORTED RESULTS:

Diazinon as a microencapsulated formula (MCAP) was adsorbed by high organic sandy loam, clay loam, and sandy loam soils at 97.9-99.9% of applied and desorbed at nondetectable - 1.5% of recovered (Table 2). Diazinon as an emusifiable concentrate (EC) was adsorbed and desorbed by high organic sandy loam soil at 97.5-98.2% of applied and 1.7-2.5% of recovered, respectively. In the clay loam and sandy loam soils diazinon (EC) was adsorbed at 56.6-74.5% of applied and desorbed at 20.8-29.3% of recovered. Soil extraction by acetonitrile yielded 56.5-106.6% of recovered diazinon in all three soils for both formulations.

- The test substance was the formulated product and not technical grade or purer.
- 2. The high organic soil was referred to as a muck soil in the study but according to the USDA soil classification system it is a sandy loam soil.
- Values of soil/water relationship (K_d) were not reported.

Table 1. Soil characteristics.

Location	Soil type	Sand	Silt	Clay	Organic matter	рH	CEC (meq/100 g)
CA	Sandy loam	62	24	14	0.9	5.7	6.6
.PA	Clay loam	41	31.1	27.8	2.1	7.2	20.8
NY	High organic sandy loam	70.0	29.2	0.8	`7 . 8	7.5	74.4

SHO

Table 2. Diazinon adsorbed (% of applied), desorbed, and acetonitrile extracted (% of recovered) in high organic sandy loam, clay loam and sandy loam soils treated with diazinon EC or MCAP at ~2, 5, 10, and 20 ppm.

		MCAP	(ppm)			EC	(ppm)	
	2	5	10	20	2	5	10	20
-			ligh organ	nic sandy	loam			71 is
Adsorbeda Desorbedh Extracted	99.6 0.09 97.2	99.6 None ^c 95.3	99.5 0.5 89.1	99.9 0.09 103.7	97.8 1.7 88.0	98.2 1.7 94.9	97.6 2.5 95.9	97.5 2.1 106.7
é			<u>C1a</u>	y loam				
Adsorbeda Desorbedb Extracted	99.5 0.3 86.5	99.4 0.2 92.7	99.5 0.6 96.7	99.7 0.3 106.6	74.5 26.0 93.7	69.7 23.9 88.3	69.9 21.4 82.7	68.7 21.7 94.0
			San	dy loam				
Adsorbeda Desorbed ^b Extracted ^d	98.9 1.0 96.7	99.3 0.5 91.7	97.7 1.5 102.4	99.1 0.6 101.4	65.9 28.7 97.5	67.0 29.3 84.6	68.9 20.8 74.8	56.6 27.9 97.4

a Adsorption in % of applied diazinon.

h Desorption is % of diazinon recovered from the adsorption process.

^C Detection limit was not specified.

d Extraction of soil with acetonitrile.

CASE GS0238 DIAZINON STUDY 13 PM --CHEM 057801 Diazinon BRANCH EAB DISC --FORMULATION 04 - GRANULAR (G) FICHE/MASTER ID 00092960 CONTENT CAT 01 Burkhardt, C.C., and M.L. Fairchild. 1967. Bioassay of field-treated soils to determine bioactivity and movement of insecticides. J. of Econ. Entomol. 60(6): 1602-1610. Also In unpublished submission received Sept. 8, 1970 under unknown admin. no.; submitted by American Cyanamid Co., Princeton, NJ; CDL:120350-C. SUBST. CLASS = S. DIRECT RVW TIME = 4 (MH) START-DATE END DATE REVIEWED BY: J. Blake
TITLE: Staff Scientist ORG: Dynamac Corp., Rockville, MD TEL: 468-2500 APPROVED BY: A. Abramovitch TITLE: Chemist ORG: EPA TEL: 557-1975 SIGNATURE: DATE: MAR 28

CONCLUSION:

Field Dissipation - Terrestrial

This study is unacceptable and does not fulfill EPA Data Requirements for Registering Pesticides because a nonspecific bioassay was used.

MATERIALS AND METHODS:

Diazinon (14% G, American Cyanamid Co.) was banded (7-inch band) onto field plots of Wabash silty clay (site 2) and Buckner silty clay soils (Table 1) at 1 and 2 lb ai/A, respectively, and onto Wabash silty clay (site 1), Wabash silt loam, and Mexico silty clay loam soils (Table 1) at 1, 2, and 4 lb ai/A. Four replicate plots were prepared for each treatment. The study was conducted at several sites in Missouri; applications were made in the spring of 1965 or 1966. Soil cores (3.5 inches in diameter, either 3 or 5 inches deep) were taken immediately after treatment and at 1, 2, 4, 6, and 8 weeks thereafter. Soil core samples were taken from the center of the band in all plots, and core samples of soil approximately 2 inches outside the band were removed from the plots of Wabash clay loam (site 1) and Wabash silt loam soils. Five inch cores were divided into segments of 1- to 3, 3- to 4, and 4- to 5-inches. Like

samples in each plot were pooled for analysis. In addition, soil core samples were taken to a depth of 6 inches and sectioned into 1-inch segments to determine the extent of vertical movement of diazinon. Triplicate subsamples (3 tablespoons each) were placed in one pint plastic containers (soil saturated with water) with 21 day old house crickets (Acheta domesticus). Mortality counts were made after 48 hours.

REPORTED RESULTS:

Diazinon insecticidal residues in the top 3 inches of soil as measured by insect mortality were reduced from 100% at time zero to 73, 60, 87, and 53% in the Buckner silty clay, Wabash silty clay, Wabash silt loam, and Mexico silt loam soils, respectively, within 8 weeks (Table 2) for the highest treatment rates. Dissipation occurred more slowly at higher treatment rates; cricket mortality 8 weeks after treatment at 2-4 lb ai/A was 53-87%, while at the lower treatment rate (1 lb ai/A) mortalities were <7%. Analysis of Wabash silty clay soil (4 lb ai/A) from the 3- to 5-inch depth indicates minor leaching to 4 inches with 3 and 7% cricket mortality at weeks 3 and 5, respectively. Lateral movement of diazinon residues in the Wabash soil was not observed. In Mexico silt loam soil diazinon at 4 lb ai/A leached to a depth of 5 inches with 100% cricket mortality 4 weeks posttreatment (Table 3).

- 1. A standard curve relating diazinon concentration to cricket mortality was not established; therefore, proper assessment of diazinon dissipation from soil could not be performed. It also appears that controls were not used during the bioassay.
- 2. Because a nonspecific bioassay was used, the pattern of decline of diazinon and the patterns of formation and decline of degradates could not be assessed.
- 3. According to the USDA soil textural classification system, the test soils reported to be Buckner silt loam, Wabash clay loam, and Wabash silty clay loam soils are all silty clay soils, and the test soil reported to be a Mexico silt loam soil is a silty clay loam soil.
- 4. Preapplication soil samples were not analyzed.
- Temperature data were not reported.

Table 1. Soil characteristics.

Soil type	Sand	Silt	Clay ·	Organic matter	рН
Buckner silty claya	6.4	52.1	41.5	4.3	5.4
Wabash silty clay ^a (Site 1)	1.4	42.6	56.0	3.6	6.5
Wabash silt loam	3.0	72.0	25.0	3.1	5.9
Wabash silty clay ^a (Site 2)	4.8	53.2	42.0	2.9	6.2
Mexico silty clay loama	2.8	67.2	30.0	2.6	4.7

a See Discussion No. 2.

Table 2. House cricket bioassay of diazinon treated field soils showing 48-hour percent mortality.a

				Samp	ling i	nterva	1	
	Treatment Rainfallb		Weeks					
Soil	rate (1b/A)	(inches)	Day 0	1	2	4	6	8
Buckner silty clay	2	6.0	100	100	100	100	100	73
Wabash silty clay (Site 1)	1	6.0	100	93	37	37	3	0
Wabash silty clay (Site 1)	2	6.0	100	100	100	100	77	0
Wabash silty clay (Site 1)	4	6.0	100	100	100	100	93	60
Wabash silt loam	1 .	7.0	100	100	100	77	30	0
Wabash silt loam	2	7.0	100	100	100	100	83	0
Wabash silt loam	4	7.0	100	100	100	100	100	87
Wabash silty clay (Site 2)	1	8.4		100	100	80	40	0.
Mexico silty clay loam	í	8.4	100	100	100	40	3	0
Mexico silty clay loam	1	8,4	100	100	100	100	0	0
Mexico silty clay loam	1	8,4	100	100	100	93	10	7
Mexico silty clay loam	2	8.4	100	100	100	100	30	0
Mexico silty clay loam	4	8.4	100	100	100	100	100	53

a Soil samples from the 1- to 3-inch depth.

b Cumulative rainfall over an 8 week period.

Table 3. House cricket bioassay of diazinon treated Mexico silty clay loam sampled to a depth of 6 inches, showing 48-hour percent mortality.

		•	· .s	ampling	interv	al	<u> </u>	·
reatment	Sampling				Week	S		
rate depth (1b/A) (inches)	Day 0	1	2	3	4	6	8	
1 1 2 3 4	1	100	160	100	100	100	0	3
	2	100	100	93	57	47	Ö	Ŏ
	3	100	100	93	70	43	Ô	3
	0	0	63	47	40	Ö	ō	
	5	. 0	0	0	0	3	Ŏ	
	6	0	0	0	Õ	ō	ŏ	0
4	1	100	100	100	100	100	100	67
	2	100	100	100	100	100	80	67
	3	100	100	100	100	100	90	70
	4	0	0	100	100	100	83	50
	5	0	Ö	0	Ö	100	3	17
	6	0	Ō	Ō	Ŏ	3	Ŏ	0

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CASE GS238	DIAZINON	STUDY 14	PM
CHEM 057801	Diazin	on	
BRANCH EAB	DISC -	-	
FORMULATION (09 - MICROENCAPSI	ULATED (MCAP); 12-EM	JLSIFIABLE CONCENTRATE (EC)
FICHE/MASTER Agchem. 198	ID 00118024	CONTENT CAT 01	dissipation: Project No. WI-5-81.
SUBST. CLASS		******	
DIRECT RVW TI	ME = 7 (MI)	CTADT DATE	
	(tut)		END DATE
REVIEWED BY: TITLE: ORG:			END DATE
REVIEWED BY: TITLE: ORG: TEL: APPROVED BY: TITLE: ORG:	G. Moore Staff Scientist Dynamac Corp., 468-2500 A. Abramovitch Chemist		

CONCLUSIONS:

Field Dissipation - Terrestrial

- This study does not fulfill EPA Data Requirements for Registering Pesticides because the test substance was uncharacterized, complete field test data were not reported, and the patterns of formation and decline of degradates were not addressed. However, the portion of the study pertaining to the California loam, the Washington sandy loam and the Pennsylvania silty loam soils provides supplemental information. The portion of the study pertaining to the Texas loam soil is unacceptable because the sampling interval is inadequate to assess the dissipation of diazinon in soil.
 - 2. Supplemental data indicate that diazinon (EC, purity unspecified) at 4.0 to 6.0 lb ai/A, declined in loam, sandy loam, and silty loam soils with a half-life of <7 days. Concentrations declined from 4.7 to 1.6 ppm (loam soil), from 3.4 to 0.30 ppm (sandy loam soil) and from 0.75 to 0.18 ppm (silty clay loam soil) by day 7. Variable concentrations of diazinon were detected at the 7.5 to 15.0 cm depth.

MATERIALS AND METHODS:

Field plots (Table 1) of turf grass in Tacoma, Washington; Fresno, California; Warminster, Pennsylvania; and Byran, Texas, were treated with diazinon (MCAP, purity and source unspecified) or diazinon (EC, purity and source unspecified) at 4.0, 5.5 or 6.0 lb ai/A. Soil samples (0- to 7.5 and 7.5- to 15.0-cm depths) were taken pretreatment, immediately posttreatment, and at intervals up to \sim 126 days and stored frozen until analysis.

The samples were analyzed for total diazinon (both formulations) by extracting with acetonitrile. After partitioning into hexane followed by column cleanup, the extracts were analyzed by GC equipped with a phosphorus specific detector. The detection limits were 0.01 ppm (total residue method) and 0.05 ppm (free residue method). Recovery from fortified samples ranged from 89-97% (total residues) and from 78-103% (free residues).

REPORTED RESULTS:

Diazinon (EC) declined in loam, sandy loam, and silty clay loam soils with a half-life of <7 days (Table 1). Concentrations declined from 4.70 to 1.60 ppm (loam), 3.40 to 0.30 ppm (sandy loam) and from 0.75 to 0.18 ppm (sitly clay loam) by day 7. Variable concentrations of diazinon were detected at the 7.5 to 15.0 cm depth. Treatment with the MCAP formulation resulted in variable concentrations being detected due to the slow release nature of the product.

- 1. Complete field test data, such as rainfall, soil and air temperature, slope, and depth to water table, were not reported.
- The test substance was applied to turf, rather than directly to the soil, which may have accounted for the flucuations in detected concentrations. In addition, translocation by the plants to the root zone may have been responsible for the presence of diazinon in the 7.5 to 15.0 cm layer.
- The patterns of formation and decline of degradates were not addressed.
- 4. The test substance was not completely characterized.



Table 1. Soil characteristics.

Source	Soil type	Sand	Silt	Clay	Organic matter	pН	CEC (meq/100 g)
Fresno, CA	Loam	42	45	13	0.8	7.4	7.2
Tacoma, WA	Sandy loam	67	32	1	4.1	6.7	12.5
Warminster, PA	Silty clay loam	9	62	29	2.0	6.1	11.7
Bryan, TX	Loam	48	39	13	1.0	6.3	11.5

Table 2. Concentrations (ppm) of diazinon in four soils planted in turf and treated with diazinon (EC) at 4-6 lb ai/A.

Sampling	Sampling	depth (cm)
interval (days)	0-7.5	7.5-15.0
	California loama	:
0 7 14 35 68 97	4.70 1.60 1.30 0.31 0.05 0.01	0.05 0.38 0.02 0.04 0.01
	Washington sandy loam	b
0 7 14 28 61 92 126	3.40 0.30 1.00 0.54 0.30 0.16 0.16	1.10 0.40 0.25 0.14 0.02 0.01
	Pennsylvania silty clay l	oama
0 7 14 26 61	0.75 0.18 0.06 0.05 ND	0.16 0.03 0.02 NDC ND
	Texas loamd	
0 7 14 28 65	0.30 0.09 0.01 0.01	0.09 0.02 ND ND

a Treated at 6 lb ai/A.

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b Treated at 5.5 lb ai/A.

C Not detected; detection limit was 0.01 ppm

d Treated at 4.0 1b ai/A.

Table 3. Concentrations (ppm) of diazinon in four soils planted in turf and treated with diazinon (MCAP) at 4-5.5 lb ai/A.

	Sampling	depth (cm)
Sampling interval	0-7.5	7.5-15.0
(days)	Total Freed	Total Free ^a
	California loamb	
0 7 14 35 68 97	6.8 3.8 1.3 1.2 1.7 0.96 2.1 0.56 0.45 0.17 0.11 NDC	0.25 0.22 0.06 0.05 0.25 0.30 0.06 0.15 0.05 0.09 0.05 NDC
	Washington sandy loam	
0 7 14 28 61 92 126	6.7 2.5 3.6 1.6 4.3 1.6 0.92 0.61 0.55 0.21 0.02 NDC 0.01	2.0 0.49 1.2 0.31 0.93 0.20 0.30 0.11 0.02 NDC NDd NDC
	Pennsylvania silty clay l	oamb
0 7 14 26 61	1.30 0.72 1.40 0.76 0.49 0.34 0.25 0.17 0.12 0.08	1.20 0.25 0.22 0.22 0.06 0.07 0.03 NDC
	Texas loame	
0 7 14 28 65	1.10 0.30 0.49 0.17 0.10 NDC 0.03	0.13 0.07 0.04 NDC 0.01 NDC

a Represents the amount of diazinon that has been released into soil.

h Treated at 5.5 lb ai/A.

C Not detected; detection limit was 0.05 ppm.

d Not detected; detection limit was 0.01 ppm.

e Treated at 4.0 lb ai/A.

CASE GS0238	DIAZINON	STUDY 15	PM				
CHEM 057801	Diazino	1					
BRANCH EAB	DISC						
FORMULATION (04 - GRANULAR (G)						
FICHE/MASTER ID 00027142 CONTENT CAT 01 Ritter, W.F., H.P. Johnson, and W.G. Lovely, et al. 1974. Atrazine, propachlor, and diazinon residues on small agricultural watersheds: Runoff losses, persistence, and movement. Environ. Sci. and Technol. 8(1):38-42. Also In unpublished submission received July 19, 1978 under 201-403; submitted by Shell Chemical Co., Washington, D.C.; CDL:234472-T.							
SUBST. CLASS	= S.						
DIRECT RVW T	ME = 3 (MH)	START-DATE	END DATE				
ORG:	J. Blake Staff Scientist Dynamac Corp., F 468-2500		•				
TITLE: ORG:	A. Abramovitch Chemist EPA 557-1975		_				
SIGNATURE:	Shamortel		DATEMAR 28 300				

CONCLUSIONS:

Ancillary - Soil Runoff

- This runoff study is unacceptable since it cannot be properly evaluated for lack of sufficient experimental information such as, rainfall, purity and soil characteristics (see Discussion for additional information). The Ecological Effects Branch has concerns about soil runoff. Therefore, a new study should be submitted to EAB for evaluation.
- 2. Diazinon (purity unspecified) at 1 lb/A dissipated from silt loam soil (10-15% slope) in the water and sediment with maximum concentrations of 82 ppb and 0.17 ppm, respectively. Diazinon was detected in the soil at <1 ppm a few hours after application, and was not detectable (<0.1 ppm) after 21 days.

MATERIALS AND METHODS:

Measurements of diazinon in soil and surface runoff from four agricultural watersheds (1.3-3.8 A) in Iowa were made from 1967 to 1970. Silt loam soil (soil not further characterized) was the predominant soil type in each watershed (slope of 10-15%); one watershed was

ridged, the other surface-contoured. Both were planted to corn in all 4 years. Diazinon (G, purity and source unspecified) was applied 1-2 inches deep to the watersheds yearly at 1 lb/A at the time of first cultivation. Propachlor (WP, purity and source unspecified) was applied to two of the watersheds at 4 and 6 lb/A in 1967-1968 and 1969-1970, respectively. Atrazine (WP, purity and source unspecified) was applied to the other two watersheds at 2 and 3 lb/A in 1967-1968 and 1969-1970, respectively. The amount of active ingredient applied per acre was not specified.

Water and sediment samples were collected in glass bottles using single-stage sediment samplers. The samples were subsequently transferred to polyethylene bottles and frozen until analyzed. Water and sediment samples were analyzed for diazinon in 1968 and 1969. Soil samples were taken to a depth of 5 inches, 24 hours after application, and at 7 day intervals for 4-6 weeks after application. Late fall samples were taken at depths of 6-8 and 8-10 inches. Seven and six sampling sites within the surface-contoured and ridged watersheds were sampled, respectively. Multiple core samples were composited from various sites within a sampling grid for each watershed.

Water samples were extracted twice with hexane. The hexane extracts were combined, concentrated, and an aliquot was analyzed using GC. Soil samples were extracted with acetonitrile, filtered, and an aliquot of the extract was analyzed for diazinon using GC. Recovery from fortified samples averaged 78% in water and 63% in soil. The detection limits were 0.01 and 0.1 ppm for water and soil, respectively.

REPORTED RESULTS:

Diazinon was detected in 29% of the water samples with a maximum concentration of 82 ppb. Diazinon was detected in 44% of the sediment samples with a maximum concentration of 0.17 ppm. The highest diazinon concentration (0.1% of applied) occurred in water and sediment samples taken 4-10 days posttreatment when a rainstorm occurred 4 days after application. Diazinon was detected at low levels in the soil with <1 ppm detected a few hours after application. Diazinon was not detectable (<0.1 ppm) 21 days posttreatment.

DISCUSSION:

- 1. Soil characteristics, such as organic matter content, pH, and CEC, and water table and meteorological data, were not provided.
- 2. The application rate was not specified in terms of the active ingredient.
- 3. Runoff was not defined as a volume of water, therefore, the total loss of diazinon in runoff could not be confirmed.
- 4. No pretreatment soil samples were taken to establish the background level of diazinon in the soil.



CASE GS0238 DIAZINON STUDY 16 PM --CHEM 057801 Diazinon BRANCH EAB DISC --FORMULATION 90 - FORMULATION NOT IDENTIFIED FICHE/MASTER ID 00103643 CONTENT CAT 01 Kadoum, A., T. Hopkins, and H. Knutson. 1969. Reduction of hazards associated with the presence of residues of insecticidal chemicals in the environment: NC-85. Progress rept., Oct. 16, 1969. Unpublished study received on unknown date under 9F0786; prepared by Kansas State Univ., Agricultural Experiment Station, Dept. of Entomol., submitted by Shell Chemical Co., Washington, DC; CDL:095474-F. SUBST. CLASS = S. DIRECT RVW TIME = 2 (MH) START-DATE END DATE REVIEWED BY: J. Blake TITLE: Staff Scientist ORG: Dynamac Corp., Rockville, MD TEL: 468-2500 APPROVED BY: A. Abramovitch TITLE: Chemist ORG: EPA TEL: 557-1975 SIGNATURE: DATE: MAR 23 TOS

CONCLUSION:

Field Dissipation - Terrestrial

This study is unacceptable because the analytical method was not described and the sampling intervals were inadequate to accurately assess the dissipation of the test substance from soil. In addition, this study would not fulfill EPA Data Requirements for Registering Pesticides because the test substance and soil were uncharacterized, complete field test data were not reported, and degradates were not characterized.

MATERIALS AND METHODS:

A plot (3 A) of Harney silt loam soil (soil not further characterized) near Cedar Bluff, Kansas, was treated with diazinon (test substance uncharacterized, source unspecified) at various rates (Table 1) between the years 1966 to 1969 at planting time (corn) and once during the growing season. Duplicate soil core (0.75 inches, diameter) samples were taken to a depth of 6 inches in and between rows, and packed in dry ice until analysis. Soil samples were screened (0.25 inch mesh), mixed, and 400 g subsamples were analyzed by an undescribed method.



REPORTED RESULTS:

Water on the plot from rainfall and irrigation averaged ~50-60 inches per year.

Diazinon residues were not detected (detection limit was 0.01 ppm) in the silt loam soil, except in samples taken immediately after treatment at planting (Table 1).

DISCUSSION:

- The analytical methods were not described.
- The sampling interval (one sample at planting, midseason, and at harvest) were inadequate for accurate assessment of pesticide dissipation from soil.
- The test substance was uncharacterized.
- 4. Complete soil characteristics, such as textural analysis, organic matter content, pH, and CEC, were not reported.
- Complete field test data, such as air and soil temperatures, techniques of planting and harvesting, slope of plots, and depth to the water table, were not reported.
- 6. Degradates were not identified.

CASE GS0238 DIAZINON STUDY 17 CHEM 057801 Diazinon BRANCH EAB DISC --FORMULATION 90 - FORMULATION NOT IDENTIFIED FICHE/MASTER ID 00120421 CONTENT CAT 01 Lichtenstein, E.P., T.W. Fuhremann, and K.R. Schulz. 1968. Effect of sterilizing agents on persistence of parathion and diazinon in soils and water. J. Agric. Food Chem. 16(5):870-873. SUBST. CLASS = S. DIRECT RVW TIME = 4 (MH) START-DATE END DATE REVIEWED BY: J. Blake TITLE: Staff Scientist ORG: Dynamac Corp., Rockville, MD TEL: 468-2500 APPROVED BY: A. Abramovitch TITLE: Chemist ORG: EPA TEL: 557-1392 SIGNATURE: DATE: -

CONCLUSIONS:

Metabolism - Aerobic Soil

This portion of the study is unacceptable because the sampling interval (one sample) was inadequate, and the method was not described in sufficient detail to adequately assess the degradation of the test substance in soil. In addition, this portion of the study would not fulfill EPA Data Requirements for Registering Pesticides because the soil was incompletely characterized, the test substance was uncharacterized, degradates were not identified, a material balance was not provided, and the incubation temperature was not reported (Experiment 1).

Degradation - Hydrolysis

This portion of the study is scientifically invalid because sterility was not maintained during the study since sterilization with NaN3 was ineffective. In addition, this portion of the study would not fulfill EPA Data Requirements for Registering Pesticides because the data was based on an unacceptable analytical method (fly mortality), the purity of the test substance was unspecified, the test solutions were not buffered, the degradates were not quantified, material balance was not provided, the study was conducted for an insufficient length of time and the half-life of diazinon was not determined and the amount of cosolvent (acetone) was unspecified.

Sac

MATERIALS AND METHODS:

Metabolism - Aerobic Soil

Experiment 1

Carrington silt loam soil (soil not further characterized) was treated with diazinon (test substance uncharacterized, source unspecified) at 1 ppm. Aliquots (400 g) of the treated soil were placed in glass columns (7 cm i.d. x 60 cm height) and water, water plus 0.1% linear alkyl benzene sulfonate (LAS), or water plus 0.1% sodium azide (NaN3) was added until the soil was saturated. The columns were incubated in the dark for 17 days, then the treatment solutions (water, water plus LAS, water plus NaN3) were percolated through the columns until 300 ml of each were collected. The soil was removed from the columns and dried to field capacity. The percolated and soil were extracted and analyzed by a referenced (not provided) method (Lichtenstein, E.P., T.W. Fuhremann, K.R. Schulz, and R.F. Skrentny. 1967. J. Econ. Entomol. 60:1714-21).

Experiment 2

Aliquots (140 g) of loam soil (soil not further characterized) were treated with water (7 ml) or aqueous solutions (7 ml) of sodium a zide (0.05% of soil weight), LAS (0.42% of soil weight), or autoclaved (6 hours per day for 5 days). The soil was placed in jars and treated with diazinon (test substance uncharacterized, source unspecified) at 10 ppm. The jars were plugged with cotton and incubated at 30°C for 7 days, after which an additional 7 ml of each of the treatment solutions (water, water plus NaN3, or water plus LAS) was added to their respective jars. The jars were incubated again for 7 days and the soils were extracted and analyzed by the method referenced in Experiment 1.

Degradation - Hydrolysis

Flasks of distilled water were treated with ring-labeled [14c]diazinon (specific activity 4.0 microCi/mg, purity unspecified, Geigy Chemical Corp.) in acetone at 10 ppm, or ring-labeled [14c]diazinon (10 ppm) plus sodium azide (0.05% of the water), or ethoxy-labeled [14c]diazinon (specific activity 4.3 microCi/mg, purity unspecified, Geigy Chemical Corp.) in acetone at 10 ppm, or ethoxy-labeled diazinon (10 ppm) plus sodium azide (0.05% of the water), or distilled water plus 0.05% sodium azide. All flasks were glass stoppered and incubated in the dark at 30°C for 14 days.

The test solutions were sampled at 8 and 14 days and extracted with hexane. The hexane extract residue was dried and exposed to Vinegar flies (Drosophila melanogaster Meig.). Fly mortality was observed after 24 or 48 hours of exposure. The test solutions were also sampled at 1, 3, and 7 days. Aliquots (25 ml) of the test solutions were extracted with hexane, dried over anhydrous sodium sulfate, and analyzed by GLC. Unextracted water samples, and the hexane and water phases of the hexane extraction were subjected to LSC. The hexane and hexane-extracted water fractions from the 7 day samples were analyzed by TLC

Table 1. Diazinon residues (ppm) in silt loam soil treated with diazinon at various rates.

	Year				
	1966	1967	1968	1969	
At planting ^a	`				
Application rate (1b/A)	0.89	0.93	2.05	1.05	
Pretreatment	NDp	••	. ND	••	
Posttreatment	0.69	3.34	0.85	0.90	
Midseason ^C		•			
Application rate (1b/A)	1.4	1.2	1.41	1.0	
Pretreatment	ND .	ND		ės	
Posttreatment	••	ND	ND	ND	
larvestd	ND .	••			

a Pretreatment and immediate posttreatment samples were taken in April and ... May, respectively.

b Not detectable; the detection limit was 0.01 ppm.

^C Midseason treatment and samples were taken in June, July, and August.

d Harvest occurred in August, September, and October.

using benzene:chloroform:ethyl acetate (2:2:1) followed by spraying with 0.01% Rhodamine B in ethyl alcohol (95%), exposure to UV light, and successive sprays of 0.5% palladium chloride and 5 N sodium hydroxide. The water fraction of the hexane extract was acidified to pH 2 with hydrochloric acid, re-extracted twice with diethyl ether, and the extracts were combined and concentrated. Aliquots were spotted on silica gel TLC plates and developed using benzene:chloroform:ethyl acetate (2:2:1) or 2-propanol:ammonium hydroxide (8:2). The plates were sprayed and handled as described above. All plates were autoradiographed for 60 hours and comparison was made to standards.

REPORTED RESULTS:

Metabolism - Aerobic Soil

Experiment 1

Dia zinon at 1 ppm degraded in silt loam soil declining to 0.340, 0.026, and 0.285 ppm when percolated through the soil with water, water plus NaN3, and water plus LAS, respectively (Table 1). Diazinon in the percolate was detected at low levels (trace amounts to 0.016 ppm).

Experiment 2

Diaginon at 10 ppm degraded in loam soil after 14 days, declining to 31.1%, not detectable, 52.7% and 28.6% of applied when treated with water, water plus NaN3, water plus LAS, or in autoclaved soil, respectively (Table 2).

Degradation - Hydrolysis

Vinegar flies exposed to the hexane extract of the $[^{14}C]$ dia zinon-only treatment taken at 8 and 14 days, showed 100% mortality within 20 minutes. However, for the $[^{14}C]$ dia zinon plus NaN₃ treatment there was 90% Vinegar fly mortality in 24 hours of exposure to the 8 day sample, and no mortality in 48 hours of exposure to the 14 day sample. No mortality was observed after 24 hours of exposure to the hexane extracts of the water-only, or the water plus NaN₂ treatments.

Ring-labeled and ethoxy-labeled [14c]dia zinon at 10 ppm degraded in an aqueous solution (pH 4.9), declining to about 7.5 ppm in 7 days when incubated in the dark at 30°C (Figure 1). When sodium a zide (NaN3) was added, [14c]dia zinon degradation was accelerated, declining to 0.2 ppm in 7 days. Degradates detected in the water and hexane phases following hexane extractions were 0'-0-diethylthiophosphoric acid, 2-isopropyl-4-methyl-6-hydroxypyrimide, a water soluble hydroxypyrimidine compound, and two other unknowns. The degradates were not quantified.

DISCUSSION:

Metabolism-Aerobic Soil

- 1. The method was not described in sufficient detail and sampling intervals were inadequate to assess the fate of diazinon in soil.
- 2. Material balance was not provided.
- 3. The test sustance was not fully characterized.
- 4. The soil was not completely characterized.

Degradation-Hydrolysis

- 1. Analytical methods based on fly mortality are unacceptable.
- 2. Degradates were not quantified and material balance was not provided.
- 3. Buffers were not used.
- 4. The purity of the test material was not specified.
- 5. Sterilization with NaN3 was ineffective.
- 6. The amount of co-solvent (acetone) was unspecified.
- 7. The hydrolysis temperature should be 25°C±1 rather than 30°C (However, this point alone would not be reason to reject the study).
- 8. The hydrolysis half-life was not determined.



Table 1. Diazinon (ppm) in the soil and water (percolate) from columns of silt loam soil treated with diazinon at 1 ppm, or diazinon (1 ppm) plus sodium azide (NaN3), or diazinon (1 ppm) plus linear alkyl benzene sulfonate (LAS), and incubated for 17 days in the dark.

	Diazinon	(ppm)
Treatmenta	Percolateb	Soil
dater	0.012	0.340
Water plus NaN ₃ (0.1%)	Trace ^C	0.026
later plus LAS (0.1%)	0.016	0.285

 $^{^{\}rm a}$ Diazinon at 1 ppm was added to all treatments. Soil were saturated with water, water plus NaN3 (0.1%), or water plus LAS (0.1%) immediately after diazinon treatment.

b After 17 days the treatment solutions were percolated through the columns until 300 ml was collected.

C Detection limit was not specified.

Table 2. Niazinon (% of applied, % of control) in loam soil treated with diazinon at 10 ppm, or diazinon (10 ppm) plus sodium azide (NaN3), or diazinon (10 ppm) plus linear alkyl benzene sulfonate (LAS), and incubated in the dark at 30°C for 14 days.

	·	Treatment			
	Control ^a	NaN3 ^b	Autoclaving ^C	LAS ^d	
Diazinon	`				
% of Applied	31.1	NTe	28.6	52.7	
% of Control .	100.0	••	91.0	169.0	
<u>Microorganisms</u> f	7.2M	620T	100	190M	

a Control; soil treated with diazinon at 10 ppm and water only.

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 $^{^{\}rm b}$ Sodium azide (NaN3) added to soil at time of diazinon application at a rate of 0.05% of soil weight.

^C Soil autoclaved (6 hours per day for 5 days) prior to diazinon application.

d LAS added to soil at time of diazinon treatment at a rate of 0.42% of soil weight.

e Not detected; detection limit not specified (GLC).

f Total number of bacterial per gram of dry soil (T = thousand, M = million).

MATERIALS AND METHODS:

Aliquots (200 g) of a sandy loam soil from Les Barges, Switzerland (47% sand, 49.1% silt, 3.9% clay, 1.1% organic matter, 7.3 meg/100 g CEC, pH 7.5, 31% moisture at field capacity) were fortified with [14c]dia zinon (labeled at the number 2 position in the ring, 12.7 microCi/mg specific activity, 97% pure) in an acetone: water solution at 10 ppm. Each treated sample was moistened to 75% of field capacity with distilled water and was then installed in a aerated incubation apparatus. The incubation system was aerated continuously, with the off gases passing through ethylene glycol, H2SO4 and NaOH traps. All samples were maintained at 25°C in the dark throughout the study. The water content of each soil sample was measured and adjusted if necessary once a week. Gas trapping solutions were monitored for radioactivity every 2 weeks. Soil samples were removed for analysis 0, 14, 28, 56, 84 and 166 days posttreatment. The total 14C-activity in each soil sample was quantified by combusting a subsample and counting (LSC) the radioactivity released. A second aliquot of each sample was extracted five times with methanol: water (8:2). The combined extracts were concentrated and then partitioned with methylene chloride to yield an aqueous phase (Fraction A) and a solvent phase (Fraction B). The extracted soil was reextracted with methanol using a Soxhlet apparatus (Fraction C). The soil remaining after extraction was assayed for residual 14C-activity by combustion.

All extracts (Fractions A, B, and C) were subjected to TLC analyses (silica gel plates) using ethyl acetate:ethanol:ammonia (16:3:1) and ethyl acetate: acetone (1:1) as solvent systems. Non-radioactive reference materials were located on the TLC plates by viewing under UV light or by exposure to iodine vapors. Radioactive spots were located using a radiochromatogram scanner. luc-Activity in individual spots was quantified using peak areas from the radiochromatogram scanner or by scraping and counting (LSC). Gas-liquid chromatography using a flame ionization detector and a radioactivity monitor was used to verify the identity of the parent, 2-isopropyl-4-methyl-6-hydroxy-pyrimidine (IMHP), and 2-(1'-hydroxy-1'-methyl)ethyl-4-methyl-6-hydroxyprimidine (GS-31140). The IMHP metabolite was also verified by GLC/MS.

Radioactivity in the gas scrubbing solutions (ethylene glycol, H_2SO_4 and NaOH) was quantified using LSC.

REPORTED RESULTS:

Diaginon breakdown was rapid; after 14 days incubation only 12.3% of the applied $^{14}\mathrm{C}$ was associated with diaginon and 72.9% with the major degradate (IMHP) (Table 1). Cleavage of the phosphate ether linkage is presumed to be the primary route of breakdown. Breakdown of IMHP was more gradual than that of diaginon and 49% of the applied radioactive material was in the form of IMHP after 84 days. After 166 days the amount of IMHP decreased to 4.7% of the applied material. Increased recoveries of $^{14}\mathrm{CO}_2$ (55.6% after 166 days) and unextracted $^{14}\mathrm{C}$ residues (15.1% after 166 days) corresponded to IMHP breakdown. No other major metabolites were found. Radioactivity in the $\mathrm{H_2SO_4}$ and ethylene glycol traps was (1% of the applied $^{14}\mathrm{C}$ throughout the study.



Table 1. Distribution of 14C in soil treated with ring-labelled [14C]diazinon.

Tananahaa 2.5	 	Percent of applied radioactivity					
Incubation time (days)	Diazinon	IMHP	GS-31144 ^a	¹⁴ ∞ ₂	Non-extractable	Total	
0	101.6	3.1	ND		0.4	105.1	
14	12.3	72.9	ND	2.6	4.2	92.4	
28	5.3	55.9	ND	6.9	5.5	74.0	
56	3.2	69.6	ND	15.9	9.1	98.0	
84	2.0	49.0	ND	20.4	9.1	81.4	
166	0.3	4.7	1.5	55.6	15.1	82.8	

a 2-Isopropyl-4-methyl-6-hydroxypydimidine.

b 2(1'-hydroxy-1'-methyl)ethyl-4-methyl-6-hydroxypyrimidine.

DISCUSSION:

- 1. The above study satisfied EPA Aerobic Soil Degradation Data Requirements for Registration only when considered with other aerobic soil metabolism studies (see conclusion 1).
- 2. The degradation half life of diazinon to IMHP of 11 days as reported by the study author appears reasonable based on the data in Table 1. However, a value of 23.7 days was obtained by regression analysis and in absence of additional data points from day 0 to 30, the half life of diazinon cannot be accurately determined. However, other studies support a half life of 3-8 weeks.
- 3. The properties of the Swiss soil used were not compared to those of any US soils and it is not known if the rate of diazinon application is adequate for its intended use. However, these questions will be answered by field dissipation studies in US soils.
- 4. The material balance shown in Table 1, was considered acceptable by the reviewer considering the length of the study and the fact that precautions were taken to account for volatiles.

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C Includes ¹⁴C recovered as an unknown metabolite and volatile ¹⁴C compounds trapped in ethylene glycol and H₂SO₄.

DATE: 7/16/86

CASE GS 0238 DIAZINON STUDY 19 PM --CHEM 057801 Dia zinon BRANCH EAB DISC -**FORMULATION** FICHE/MASTER ID 00153973 CONTENT CAT Clint S. Skinner and Wendell W. Kilgore. 1982. Application of a Dermal Self-Exposure Model to Reentry. J. Toxicol. Environm. Health 9:461-481. SUBST. CLASS = S. DIRECT RVW TIME = 3 (MH) START-DATE 7/14/1986 END DATE 7/16/1986 REVIEWED BY: James D. Adams TITLE: Chemist ORG: Exposure Assessment Branch, HED TEL: 557-4368 APPROVED BY: Carolyn K. Offutt TITLE: Chief ORG: Environmental Processes and Guidelines Section TEL: 557-7347

CONCLUSION:

SIGNATURE:

1. This study/paper does not satisfy EPA Data Requirement for Exposure: Reentry Protection.

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2. It does contain data that show that dermal exposure of mice to dia zinon dislodgeable residues on leaves causes greater cholinesterase inhibition than exposure to similar residues of Parathion, Parathion-methyl, Azinphos-methyl, or Mevinphos. This implies greater dermal absorption and/or lesser metabolism for Dia zinon than these other highly dangerous organophosphorus (OP) insecticides.

MATERIALS AND METHODS:

This paper is essentially a modification of an animal model originally proposed by Guthrie et al. (1974. Arch. Envirorm. Contam. Toxicol. 2:233-242.) and an implementation of the model by laboratory investigation with five organophosphorus insecticides - Dia zinon, Parathion, Parathion-methyl, Azinphos-methyl, and Mevinphos. The model/method consists of exposing mice to pesticide treated leaves daily for 10-hour periods and taking blood cholinesterase enzyme activity measurements afterwards. The method does not measure exposure - only an acute effect caused by mouse exposure to leaves with known dislodgeable residue levels. The method only addresses cholinesterase inhibition resulting from dermal exposure to dislodgeable residues of these five OP pesticides.



REPORTED RESULTS:

The results of this study are of limited value. They are certainly not useful for the establishment/calculation of reentry intervals as detailed in Subdivision K. All of these studies are laboratory studies rather than studies in the environment and the data does not allow the estimation of fieldworker exposure.

DISCUSSION:

- 1. The above study does not satisfy EPA Reentry Data Requirements for Registration.
- 2. The study contains some peripherally interesting information, but otherwise, it does not provide useful data for the estimation of fieldworker exposure to residues of diazinon nor the calculation of a reentry interval.

NA

CASE GS0238	DIAZINON	STUDY 20	PM
CHEM 057801	Diazinon		
BRANCH EAB	DISC —	•	•
	DIENT-Radiolabelled 19.8 uCi/mg with 99 ID 401015-1	75 (11) 11.0/-	ta-14C-diazinon) with a specific
DAS, Y.T. 1985-E-044 SP.	987. Aquatic Anaer Unpublished study	obic Soil Metabo prepared by Bio	olism of Diazinon, Project No.
SUBST. CLASS			
DIRECT RVW T	IME = 5 (MH) S	TART-DATE	END DATE
	C. Eiden Chemist US EPA 557-0372	F. man	la, Brank Shiffer - 3/24/88
APPROVED BY: TITLE: CRG: TEL:	P. Holden Chief US EPA (703) 557-7328	et. yohus	la, March Chief
SIGNATURE:			DATE:MAR 28 300
			*

CONCLUSIONS:

Metabolism-Aquatic Anaerobic Soil:

- 1. This aquatic anaerobic soil study is acceptable and satisfy EPA Data Requirement for Registering Pesticides.
- 2. Diazinon degraded to oxypyrimidine. Only one unknown degradate was observed reaching a maximum of 3.2% of the applied Cl4 dose. The half-life for diazinon was 4 days. Oxypyrimidine reached a maximum of 50% of the 14C dose at 9.2 days, and kept increasing reaching 54% of the 14C dose in 15 days, and at the study's end (366 days) accounted for 55% of the original 14C dose.

Diazinon incubated under strictly anaerobic conditions degrades to oxypyrimidine and bound residues.

Incubated under strictly anaerobic conditions, oxypyrimidine appears to accumulate and persist. Oxypyrimidine accounted for 55% of the 14C dose at 366 days. The percentage of unextractable 14C activity at 366 days was 45%.

MATERIALS AND METHODS:

Sediment and water from a cranberry bog were taken in Wareham, Massachusetts from a field not in production. Water and sediment were placed in mason jars, sealed, and placed inside an ice-cooler and shipped for treatment at the laboratory.

The sediment was characterized as sandy:

Type	% s, s, c	pH	%OM	GEC
sand	 88,6,6	5.0	2.9	4 meq 100 g

Each reaction flask contained 25 g of sediment plus 70 ml of natural water. Individual reaction flasks were connected in series with tygon tubing for volatile traps and incubation in the dark at 25 ± 1 °C. The traps were ethylene glycol, 1 N H₂SO₄, and 1 N NaOH. Nitrogen gas was used to purge the flask systems daily to maintain anaerobic conditions. Each reaction flask was dosed with 10.5 ppm diazinon.

Upon analysis the aqueous layer was decanted and 10 g of sediment was removed and shaken on an orbital shaker with methanol:water (9:1) for 15 minutes at 270 rpm. The mixture was filtered and the soil cake washed and air-dried. Extracts of the soil were radioassayed by a liquid scintillation counter (ISC). Air-dried soils were combusted for ¹⁴C analysis in triplicates.

The methanol:water soil extracts were spotted on silica gel thin layer chromatography (TLC) plates and developed in toluene:chloroform:ethanol: formic acid (8:8:2:1). The distribution of radioactivity was quantitated with a linear image analyzer. Diazinon, oxypyrimidine and GS-31144 were used a reference compounds for identification.

50 ml of the decanted aqueous layer was removed and partitioned twice with 25 ml of dichloromethane. The aqueous and combined organic extracts were radioassayed by lsc. Extracts were applied to tlc plates and analyzed as described for the soil extracts.

Triplicate 1 ml aliquots from the trapping solutions were radioassayed by lsc.

REPORTED RESULTS:

Throughout the study period, 14 C activity partitioned between soil and water phases with means of $49.8 \pm 8.4\%$ in soil and $36.9 \pm 10.2\%$ in the water phases and <0.1% volatiles at all sampling intervals.

In this study system with a pH of 5.0, diazinon degraded rapidly to oxypyrimidine. Oxypyrimidine partitioned between the soil and water phases as follows: at 366 days, 20.4% in the soil, and 35.3% in the water. Oxypyrimidine shows a greater concentration in the water media than in the soil media, indicating mobility. (Previous studies on the mobility of diazinon indicate that under the aged-leaching studies, oxypyrimidine did leach accounting for 13-15% of the ¹⁴C dose in the column leachate.)

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Biospherics Project No. 85E-044AM/Anaerobic Final Report/February 26, 1987

Table 1. Radiocarbon Material Balance in the Diazinon Araerobic Aquatic Soil Metabolism Study

ample		Percent of App	Volatiles	Total
DAT ²	Soil ^{3,4}	Water 4	AOTECTIES	Iorai
(1)	(2)	(3)	(4)	(5)
0	40.6 (12.2)	57.3 (6.0)	<0.1	97.9
1	37.9 (11.4)	36.6 (3.8)	<0.1	74.5
25	46.5 (14.0)	32.1 (3.4)	<0.1	78.6
7	51.8 (15.5)	36.4 (3.8)	<0.1	88.2
- 15	53.4 (16.0)	34.6 (3.6)	<0.1	0.88
22	42.9 (12.9)	41.1 (4.3)	<0.1	84.0
32	48.8 (14.5)	42.0 (4.4)	<0.1	90.8
87	65.0 (19.5)	42.0 (4.4)	<0.1	107.0
183	62.9 (18.9)	14.4 (1.5)	<0.1	77.3
270	49.6 (14.9)	33.5 (3.5)	<0.1	83.1
366	48.1 (14.4)	35.6 (3.7)	<0.1	83.7
Mean	49.8 (14.9 ± 8.4 ± 2.5)	36.9 (3.8 + 10.2 ± 1.1)	<0.1	86.6 <u>+</u> 9.4

¹ Mean of 2 replications. For replicate data, see Appendix I.

2 DAT = Days after treatment.

 \mathcal{III}

³ Based on pre-extract soil combustion or methanol-water extract plus

post-extract soil combustion.

4 Numbers in parentheses indicate ppm based on soil Gry weight (µg/g) or water volume (µg/ml).

⁵ Based on Replication 1 only due to apparent error in dosing of Replication 2.

Biospherics Project No. 85E-044AM/Anaerobic Final Report/February 26, 1987

Table 2. Diazinon and its Metabolites in the Soil and Water Phases of the Diazinon Anaerobic Aquatic Soil Metabolism Study

				Correct	ed Percen	t Dose ²			
Sample	e Soil Phase			Vater Phase			Total		
DAT	Diazinon	G-27550	Unknown	Diazinon	G-27550	Unknown	Diazinon	G-27550	Unknown
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
0	22.8	4.0		55.0	• 2.2°	·	77.8	6.2	
1	25.4	10.0		30.3	6.2		55.7	16.2	-
2 ³	11.5	12.5		18.9	13.2		30.4	25.7	
7	9.4	20.2		8.0	26.7	0.8	17.4	46.9	0.8
15	3.4	22.1	***	1.3	32.2	0.4	4.7	54.3	0.4
22	1.2	17.9		1.2	36.5	1.6	2.4	54.4	1.6
32	0.3	15.0		0.1	38.6	3.2	0.4	53.6	3.2
87	0.2	23.2	-		40.8	1.0	0.2	64.0	1.0
183	-	26.6			14.4			41.0	, .
270		18.8			33.5	-		52.3	-
366		20.4			35.3			55.7	

DAT = Days after treatment.

PLG

Percent TLC peaks (Appendix II) X percent dose in water or soil extract (Appendix I) divided by 100.

³ Replication 1 only. All others are mean of 2 replications. For replicate data, see Appendix III.

Table 3. Half-bire Estimate of Diazinon
Under Anaerobic Aquatic Soil Conditions

Sample	· · ·	Radioactivity	
DAT1=x	♦ Dose ²	Relative %3	Ln of (3) = y
(1)	(2)	(3)	(4)
0	77.8	100	4.605170
1	55.7	71.6	4.271095
2	30.4	39.1	3.666122
7	17.4	22.4	3.109061
15	4.7	6.0	1.791759
	and the second s		

DAT = Days after treatment

$$T_{1/2} = \frac{\text{Ln 2}}{\text{b}} = \frac{0.693147}{0.175149} = 4.0 \text{ days}$$

Table 4. Time Estimate for Formation of G-27550 from Diazinon Under Anaerobic Soil Conditions

DAT ¹ Days = y	% Dose ²	Radioactivity Relative %	Log (3) = 2
(1)	(2)	(3)	(4)
0	6.2	. 0	0
1 .	16.2	10.0	1.000000
2	25.7	19.5	1.290035
7	46.9	40.7	1.609594
15	54.3	48.1	1.682145

¹ DAT = Days after treatment

$$T_{1/2} = [a + b(\log 50)]^3$$

= 2.095272³
= 9.2 days

r = -0.956719

y = a + bx

a = -0.142722

b = 1.317265

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² From Table 2

³ Considering 0 DAT as 100%

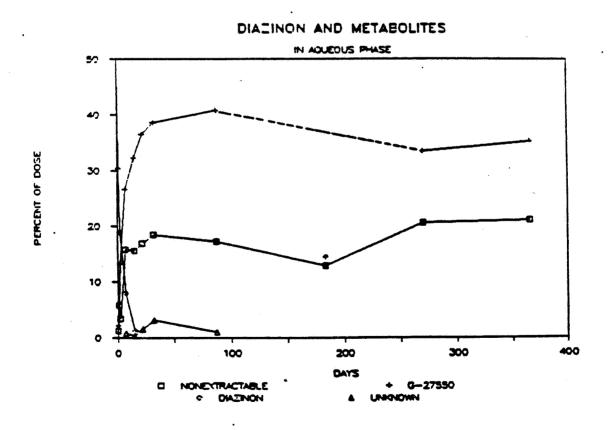
r = -0.9805y = a + bx

From Table 2

³ Considering 0 DAT as 0%

*, Position of [14C]

Figure 1. Structural Formulas of Diazinon and 2 of its Metabolites



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Figure 9. Degradation of Diazinon and Formation of its Metabolites in the Water Phase Under Anaerobic Aquatic Soil Conditions

DIAZINON AND METABOLITES

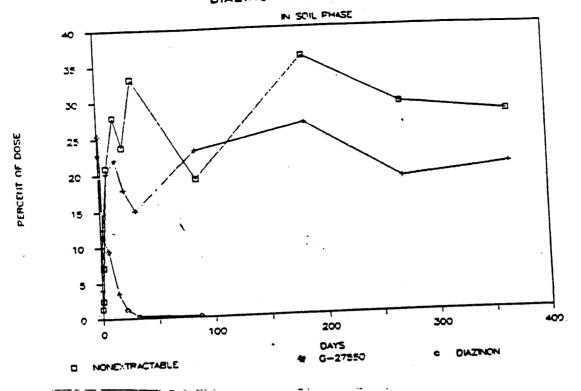


Figure 10. Degradation of Diazinon and Formation of its Metabolites in the Soil Phase Under Anaerobic Aquatic Soil Conditions

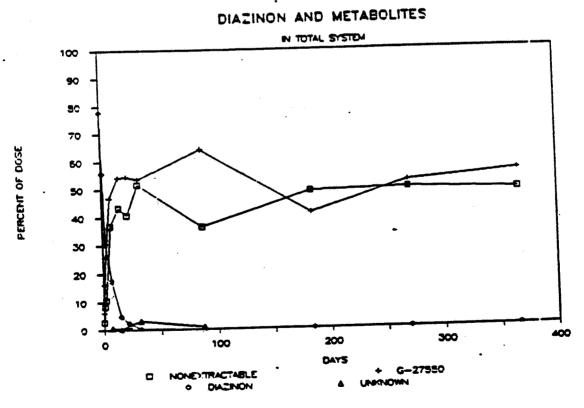


Figure 11. Degradation of Diazinon and Formation of its Metabolites in the Soil Phase and Water Phase (Combined Soil and Water Data) Under Anaerobic Aquatic Soil Conditions

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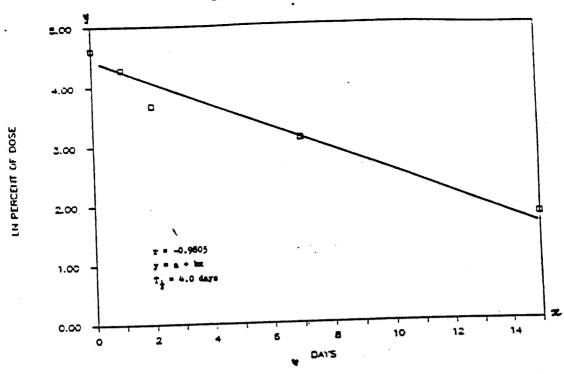


Figure 12. Kinetics of Degradation of Diazinon Under Anaerobic Aquatic Soil Conditions

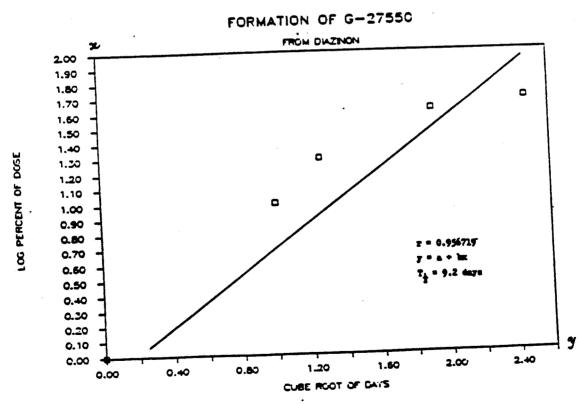


Figure 13. Kinetics of Formation of G-27550 from Diazinon Under Anaerobic Aquatic Soil Conditions

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The percentage recoveries of C^{14} material from several sampling times were averaged. They were: $86.6 \pm 9.4\%$ for the combined soil and water extracts, and $49.8 \pm 8.4\%$ and $36.9 \pm 10.2\%$ for the sediment and water extracts, respectively.

DISCUSSION:

- 1. Under strictly anaerobic conditions, diazinon, degrades to oxypvrimidine the major degradate from hydrolysis, photolysis, and aerobic and anaerobic soil metabolism. Under the anaerobic conditions, oxypyrimidine appears to accoumulate and persist. Over 50% of the diazinon applied converts to and persists as oxypyrimidine under the conditions of the study. Diazinon degrades quickly in an acidic anaerobic environment because of chemical degradation, probably hydrolysis. Acidic hydrolysis does not affect oxypyrimidine, however.
- 2. Diazinon may persist longer under alkaline anaerobic conditions. This experiment was performed under acidic conditions.

CASE @S0238 DIAZINON STUDY 21 PM ---CHEM 057801 Diazinon BRANCH EAB DISC -ACTIVE INCREDIENT-Radiolabelled diazinon (2-delta-14C-diazinon) with a specific activity of 19.8 uCi/mg with 99% purity. FICHE/MASTER ID 4002870/ DAS, Y.T. 1987. Aerobic and Anaerobic Soil Metabolism of Diazinon, Project No. 85-E-044 SP. Unpublished study prepared by Biospherics Inc. SUBST. CLASS = S. DIRECT RVW TIME = 5 (MH) START-DATE END DATE Sact. Galada, thendelle REVIEWED BY: C. Eiden TITLE: Chemist ORG: US EPA TEL: 557-0372 = Holula, Brond Chin APPROVED BY: P. Holden TITLE: Chief ORG: US EPA TEL: (703) 557-7328 DATEMAR 28 300 SIGNATURE:

CONCLUSIONS:

Metabolism-Aerobic, Anaerobic and Sterile Soil:

- This study is acceptable and satisfies EPA aerobic, anaerobic and sterile soil metabolism Data Requirement for Registering Pesticides.
- Diazinon degraded rapidly as previously reported in this review in all three study systems. Half-lives for diazinon were:

31.2 days /aerobic

34.3 days /anaerobic

46 days /sterile

Aerobic, Anaerobic, Sterile:

The major degradate was oxypyrimidine; it reached a maximum concentration in 95 days accounting for 67% of the original 14C dose in the aerobic study system.

A second degradate was identified as 2-(1-hydroxy-1-methyl)ethyl-4-methyl-hydroxypyrimidine, differing from oxypyrimidine only by an alcohol group. It reached a maximum concentration in 6 months time accounting for 12.8% of the original dose. Two unknown degradates were observed. They were not identified as they formed in amounts <1.0% of the original 14C dose in the aerobic and anaerobic study systems.

Diazinon

Microbial degradation is an important pathway of degradation for diazinon; however, as seen from the half-lives under the various study systems, degradation continues in sterile and anaerobic systems representing conditions of reduced microbial activity. The most probable mechanism responsible for degradation under these conditions is chemical hydrolysis.

Oxypyrimidine

Oxypyrimidine is more persistent than diazinon under aerobic and sterile conditions. Under anaerobic conditions, in which the parent compound (diazinon) was aged aerobically first for 32 days before establishing anaerobic conditions, it did not increase above 21.2% of the original dose of ¹⁴C and decreased to 12.7% within 30 days.

"MATERIALS AND METHODS:

The following sandy loam soil was used:

Type	% s, s, c	% OM	pН	CEC	%FC
SL	54.8,29.4,15.8	2.0	5.4	15meq 100 g	36.05

The soil was treated at 10 ppm with diazinon added to incubation flasks and incubated in the dark at 25 ± 1°C. The dosing solution consisted of 4.1 ml of sterile distilled-deionized water plus 0.5 ml ¹⁴C diazinon in dichloromethane. The incubation flasks were all equipped with gas inlet/outlet ports connected with silicone rubber tubing. Each volatile trap contained, in series, ethylene glycol, 1N H2SO4, and 1 N NaOH. Aerobic conditions were maintained by flushing with forced air. Soils for sterile incubation, were autoclaved at 15 PSI and 121°C for 60 minutes prior to dosing with diazinon. Anaerobic conditions were achieved by flooding the soil with water to a depth of 2 cm. Soils treated with diazinon were first aged aerobically for 32 days, then amended with glucose, and purged with N2 gas for the anaerobic incubation of diazinon.

At each sampling interval soils were collected in duplicate, and all trapping solutions were collected and replaced with new traps. Samples were collected on the following schedule: 0,1,3,7,14,days and 1,2,3,4,6,9, 12 months for the aerobic study system; 0,1,3,7,14 days and 1,2,3 months for the sterile study system; 1 and 2 months after aerobic incubation for 32 days for the anaerobic study system.

Aerobic

Upon sampling, the soils from each flask were removed 10g at a time and shaken with a methanol:water mixture (9:1) for 15-30 minutes on an orbital shaker. The liquid phase was filtered, and the solid soil cake rinsed and then air-dried. The liquid phase was analyzed by liquid scintillation counter (LSC), the soil cake was combusted for quantitation of bound residues.

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Anaerobic

The aqueous layer from the anaerobic flasks was decanted and radioassayed by lsc. A separate aliquot was partitioned 3 X with dichloromethane (DCM). The aqueous and organic phases were allowed to separate, and then each was radioassayed by LSC. The soil was treated as described above under the aerobic study.

Volatiles

Trapping solutions were radioassayed by LSC for all study systems.

Degradate Identification

For degradate identification, thin layer chromatography (TLC) was used. The DCM and MeOH/ H_2O extracts were spotted on TLC plates and developed in toluene:chloroform:ethanol: formic acid (80:80:20:10). The distribution of the radioactivity was quantitated by either scraping or by using a linear image analyzer.

REPORTED RESULTS:

The percentage recoveries on the methods for soil and water phases combined were for each study system: $110.5 \pm 10.6\%$, $103.4 \pm 16.5\%$, and $105.4 \pm 19.2\%$ for the aerobic, sterile, and anaerobic study systems, respectively.

Unextractable residues increased over time. Maximum amounts were reached in 3 months time. They were 35.6%, 41.9%., and 37.6% for the aerobic, sterile, and anaerobic systems, respectively.

Volatiles were not an important part of the degradation of diazinon. The traps contained $\leq 0.04\%$ of the ¹⁴C dose throughout the aerobic soil metabolism study.

Degradates and degradation rates were reported as shown on the following page:



DIAZINON

*, Position of [14c]

G27550

H3C

N
OH

GS-31144 CH3 H3C OH

TABLE 24

Kinetics of Degradation of Diazinon and Appearance of G-27550

		Diazi		G-27	7550
Test Conditions	T1/2	(days)	Unsterile/Sterile	T _{1/2} (days)	Unsterile/Steril
Unsterile aerobi Unsterile anaero Sterile aerobic		31.2 34.5 34.5 32.	8 } 0.71	56.0 57.5	0.97
Mean	1	37.2 ±7.8	·	60.1 ±5.7	
Coefficient of variation		21.0%		9.5%	

For statistical parameters, see Tables 19-23

Radiocarbon Material Balance in the Unsterile Aerobic Soil Metabolism Study Treated with ¹⁴C-Diazinon*

			Correct	ed & Dose		TLC	•
Sample	Unextractable	Diazinon	G-27550	GS-31144	Unknown I	Origin	Total
D0 D1 D3 D7 D14 D32 D64 D95 D125 D195 D281 D371	1.6 2.8 6.5 9.8 16.4 23.0 30.5 35.6 29.0 35.4 34.8 36.2	125.5 121.6 107.2 100.6 73.5 63.2 23.8 15.7 2.6 0.7 0.7	0.3 1.4 3.6 7.2 16.5 33.2 44.2 67.0 19.8 36.9 15.94	6.8 4.6 12.8 6.9	- - - - - 1.0 0.8 0.9	1.3 1.7 0.1 0 0 0.2 1.5 0.6 1.3 1.3	128.7 127.5 117.4 117.6 106.4 119.4 98.7 126.6 56.6 88.1 60.4 57.0

^{*}Adapted from Tables 3, 6, 7, 12 & 15.

TABLE 17

Radiocarbon Material Balance in the Sterile Rerobic Soil Metabolism Study Treated with 14c-Diazinon*

Sample	Unextractable	Diazinon	G-26550	GS-31144	TLC Origin	Total
D0 D1 D3 D7 D14 D32 D64 D95	1.0 3.2 5.9 10.6 22.3 25.6 38.0 41.9	103.7 132.3 96.4 100.8 92.2 69.4 37.0 29.0	0.3 1.1 2.4 6.9 16.3 23.8 33.8	0.4	7.2 0.5 0 0 0 2.2 2.2	112.2 137.1 104.7 118.3 130.8 119.2 111.0 115.2

^{*}Adapted from Tables 4, 8, 9 & 13.

*** and Unknown-II were not seen.

⁻⁸⁷⁻

Radiocarbon Material Balance in the Unsterile Anaerobic Soil Metabolism Study Treated with 14C-Diazinon*

		Corrected % Dose						
Sample	Unextra- ctable	Diazinon	G-27550	GS-31144	Un- known I	Un- known II	Tic	Total
D64					 			
Soil	29.0	13.1	18.3	0	.0	_	_	
Vater	30.6	0.5	2.9	ŏ	Ö	0	0	60.4
				•	٠.	U	0	34.0
Total	59.6	13.6	21.2	. 0	0	0	0	94.4
095								
Soil	37.6	17.5	4.5	0.1			•	
Water	23.6	0.5	8.2		0.1	0.1	0.4	60.3
		0.5	6.2	0	0	0.2	. 0	32.5
Total	61.2	18.0	12.7	0.1	0.1	0.3	0.4	92.8
						1	Hean	93.6
							•	<u>+1.1</u>

^{*}Adapted from Tables 5, 10, 11 & 14

TABLE 19

Half-life Estimate of Diazinon in Soil
Under Unsterile Aerobic Conditions

ampling Time (days) = x	Radioactivity			
	\$0	in % = y		
0	100			
1		4.605170		
3	96.9	4.572647		
7	85. 5	4.448516		
	80.1	4.383276		
32	58.5	4.069027		
54	50.3			
	19.0	3.918005		
95		2.944439		
	12.5	2.525729		

^{*} Day 0 considered as 100% from Table 7

Y = a + bx a = 4.53365

r = -0.990615

b = -0.0222171

 $rac{1}{1/2} = \frac{0.693}{h} = 31.2 \text{ days} - 88$

138

Half-life Estimate of Diazinon in Soil Under Sterile Aerobic Conditions

-14 24		Radioactivity		
ampling Time (days) = x	14	ln % = y		
0	100	4.605170		
· ·	127.6	4.848900		
<u>, </u>	93.0	4.532600		
3	97.2	4.576771		
7	88.9	4.487212		
14	66.9	4.203199		
32	35.7	3.575131		
64	28.0	3.332205		

* Day 0 considered as 100% from Table 9

$$y = a + bx$$
 $r = -0.980817$
 $a = 4.67727$
 $b = -0.015077$
 $T_{1/2} = 0.693$ = 46.0 days

TABLE 21

Half-life Estimate of Diazinon in Soil Under Unsterile Anaerobic Conditions

Sampling Time (days)		3.1	ty	
DAT	DAA ² = x	DAT	DAA ⁴	in % = y
32	6	66.2	100	4.605170
64	32	13.5	21.5	3.068053
95	63	17.9	28.5	3.349904

¹ Days after treatment (dosing).

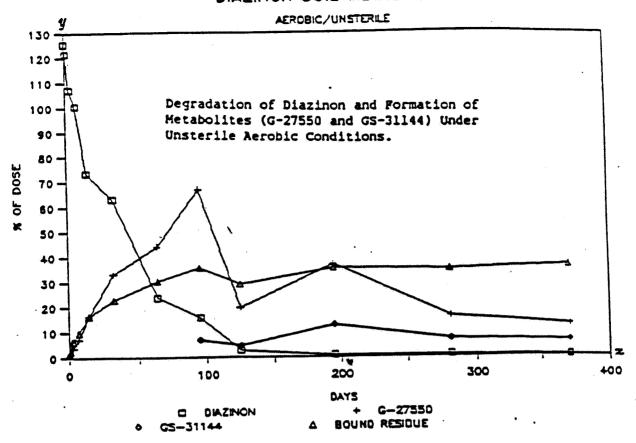
y = a + bx r = -0.772828 230 a = 4.310114b = -0.020076

 $T_{1/2} = \frac{0.693}{b} = 34.5 \text{ days}$

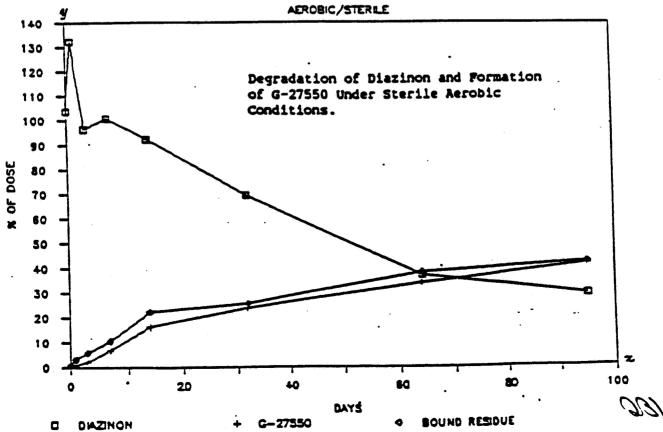
² Days after anaerobic conditions were established, i.e., after 32 days of aerobic incubation

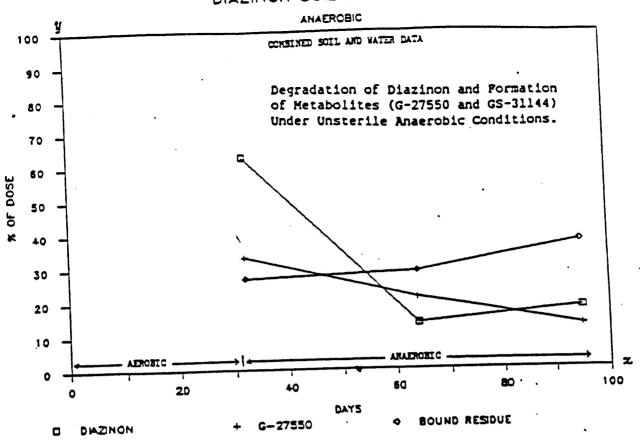
³ Based on day of treatment (day 0, aerobic) as 100% from Table 7; (64.8 divided by 97.9) 100

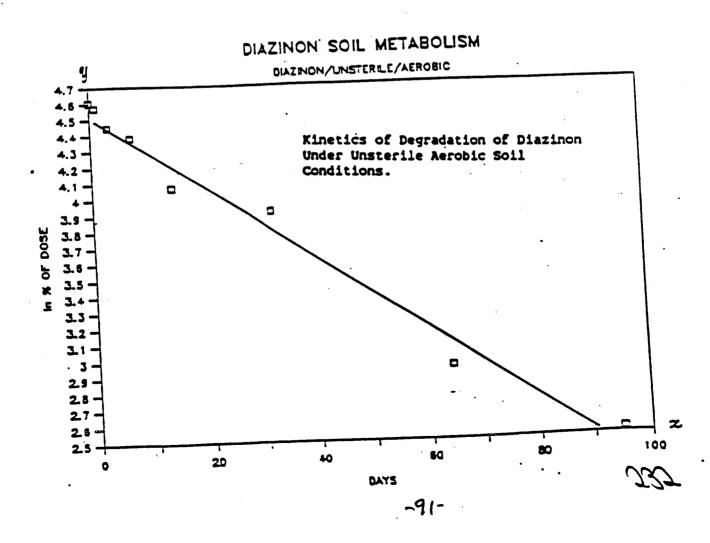
⁴ Based on 32-day aerobic (day 0, anaerobic) as 100%.

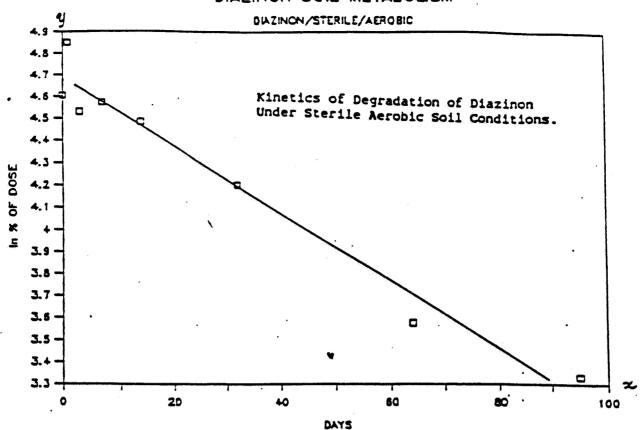


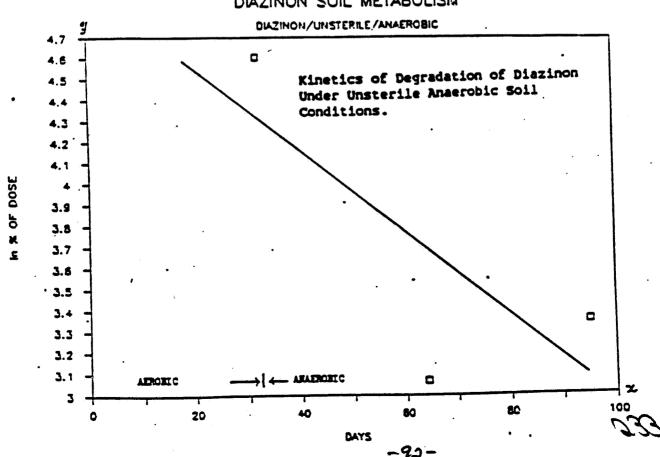


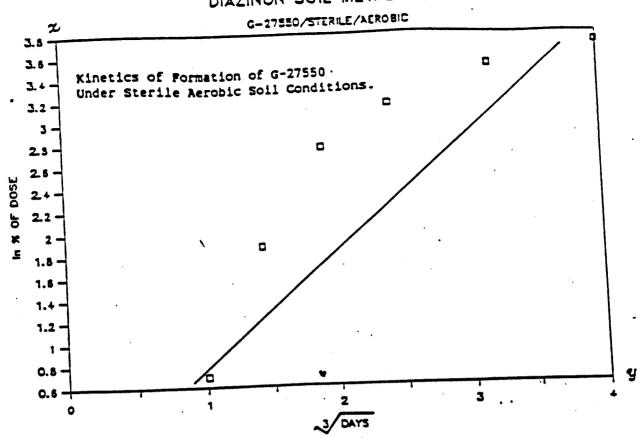


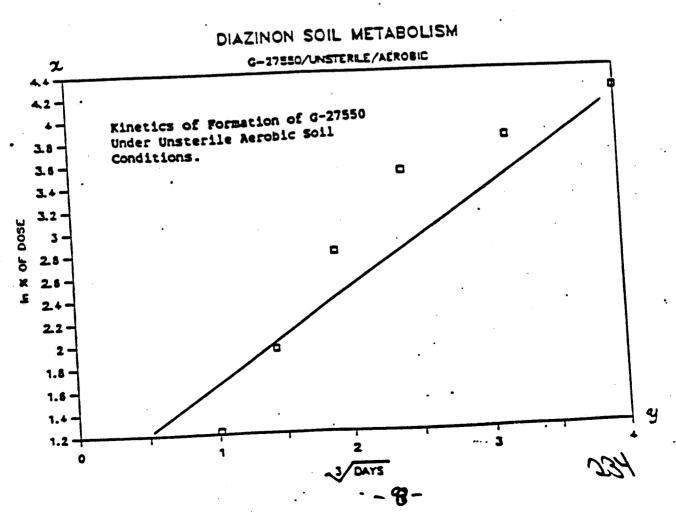












(TDRO3B)

DATA EVALUATION RECORD

PAGE 1 OF

CASE 050238

DIAZ INON

STUDIES 25

PM -

CHEM 057801

Diazinon

BRANCH EAB

DISC -

ACTIVE INGREDIENT-analytical grade ring radiolabelled diazinon of a specific activity of 36.5 uCi/mg and 98.8% radiochemical purity.

MRID 40512601

Spare, W. 1987. Leaching characteristics of diazinon. Unpublished study received Feb. 23, 1988; prepared and submitted by Ciba-Geigy Ltd., Switz.

SUBST. CLASS = S.

DIRECT RVW TIME = 5

(MH) START-DATE

END DATE

REVIEWED BY: A. Abramovitch

TITLE: Chemist ORG: US EPA TEL: 557-1975

APPROVED BY: P. Mastradone

TITLE: Acting Chief

ORG: US EPA

TEL: (703) 557-7347

SIGNATURE:

DATE:

CONCLUSIONS:

Mobility-Unaged Soil Column Leaching:

- 1. This study provides acceptable data and satisfies EPA Data Requirement for unaged leaching. Other studies provide supplemental information.
- 2. Approximately 81% of the applied unaged radioactive diazinon residues leached through a 30 cm Maryland sand column, 16% through a Maryland clay, 6% through a Mississippi silt loam and 17.5% through a California sandy loam soils with the application of 50.8 cm of water. In all cases, the predominent component in the leachate was oxypyrimidine, the primary degradate of diazinon. The parent diazinon was only present in the leachate in small amounts.

MATERIALS AND METHODS:

Analytical grade ring radiolabelled diazinon of a specific activity of 36.5 uCi/mg and 98.8% radiochemical purity was used to prepare a stock solution of diazinon in acetone of 0.00082 mg/ul. Then, 610 ul of the stock solution was added flasks and the acetone was completely evaporated. Then, 50 gm of the appropriate soils were added to each flask and the soil was roller mixed for 3 hours at 125 rev/min. The fortification level of each soil was

determined by combustion of five individual aliquots. After mixing, 10 gm samples of the fortified soils were placed at the top of the corresponding 12 inch soil columns that were segmented into 12 inch sections. Each column was then irrigated with the equivalent of 20 inches of rainfall at the rate of <1 inch/hour. Following the leaching period, the soil columns were segmented and samples from each segment was combusted for analysis. The leachate was quantified by ISC to determine the total amount of radioactive material and was retained in the refrigerator for future characterization of the leachate.

The soils used in the study are as follows:

TABLE 1: SOIL CHARACTERIZATION. FOUR SOILS USED FOR PARENT LEACHING OF DIAZINON

SOURCE MA	LRYLAND	CALIFORNIA	MARTLAND	MISS.
TEXTURE	SAND	SANDY LOAM	CLAY	SILT LOAM
ZSand ZSilt ZClay	95.6 2.2 2.2	74.0 19.6 6.4	25.2 32.8 42.0	39.5 54.2 6.3
% Organic Matter	0.9	0.5	4.8	1.0
pН	6.5	6.5	5.9	7.5
Field Capacity %	3.8	6.1	35.9	*
Cation Exchange Capacity (meq/100g) 1.8	4.7	24.3	9.7
Bulk Density (g/ml) 1.61	1.78	1.23	1.28

^{*} Soil shipped to A & L Eastern Laboratories, Inc. for moisture determination.

REPORTED RESULTS:

TABLE 2: RADIOASSAY SHOWING HOMCGENEITY OF MIXING AND DOSE CALCULATIONS

SOIL TYPE	COL. WT.G	BMO ALIQ.	LS3801 DMP	DPM/G	AVER. DMP/G	DOSE PPM	DOSE DP
BMO EFF: .9	1844						
California Sandy Loam	1\10.01 2 10.06 3 10.05	.257 .261 .259 .263 .257	170987 164816 172575 160104 170444	724404 687558 725485 662822 722103	704475	8.69	7051790 7087014 7079969
BMO EFF: .94	169			•			•
Mississippi Silt Loam	1 10.07 2 10.04 3 10.06	.266 .251 .268 .263	172201 166737 181226 172493 169155	687455 705422 718086 696476 707199	702928	8.67	7078481 7057393 7071451
BMO EFF: .91	292	•			,		
Maryland Sand	1 10.05 2 10.05 3 10.08	.253 .259 .268 .256 .262	159556 136869 141810 156156 165826	690812 578859 579614 668168 693296	642150	7.92	6453605 6453605 6472870
BMO EFF: .89	755						
Maryland Clay	1 10.07 2 10.05 3 10.03	.252 .264 .263 .261 .264	204173 161790 133074 193745 201576	902693 682794 563741 827051 850701	765396	9.45	7707539 7692231 7676923

SPEC. ACT: 36.5 uCi/mg = 81030 DPM/ug

TABLE 3: RADIOACTIVITY DISTRIBUTION PROFILE FOR MARYLAND SAND AS PERCENT OF DOSE

•	X	COLUMN		
COLUMN SECTION OR LEACHATE	#1	#2	# 3	AVERAGE
1 inch 2 3 4 5 6 7 8 9 10 11 12 TOTAL SOIL	0.53 0.21 0.26 0.27 0.53 0.71 0.93 1.41 2.53 2.57 2.96 3.75	0.82 0.21 0.14 0.22 0.30 0.52 0.99 0.99 1.99 1.85 2.20 3.53 13.75	0.52 0.18 0.25 0.19 0.33 0.58 0.60 1.03 1.59 1.53 1.97 3.06 11.83	0.62 0.20 0.22 0.23 0.39 0.60 0.84 1.14 2.04 1.98 2.38 3.45
LEACHATE COLUMN TOTAL	79.12 95.78	77.60 91.35	87.03 98.86	81.25 95.34

TABLE 5: RADIOACTIVITY DISTRIBUTION PROFILE FOR MARYLAND TLAY AS A PERCENT OF DOSE

		COLU	MIN	
COLUMN SECTION OR LEACHATE	#1	∌ 2	# 3	<u> </u>
1 Inch 2 3 4 5 6 7 8 9 10 11 12 TOTAL SOIL	58.40 5.25 1.96 1.60 1.10 1.30 1.54 1.27 0.91 1.01 1.95 2.61 78.90	54.67 6.33 1.89 1.11 1.12 1.45 1.62 1.85 1.92 1.51 1.43 1.94 76.82	63.52 4.73 4.97 3.01 3.54 3.09 2.41 1.58 0.89 0.90 0.70 0.93	58.86 5.44 2.94 1.91 1.92 1.95 1.86 1.57 1.24 1.14 1.36 1.83 82.01
LEACH COLUMN TOTAL	22.05 100.95	18.99 95.81	<u>6.97</u> 97.26	16.00 98.01

TABLE 6: RADIOACTIVITY DISTRIBUTION PROFILE FOR MISSISSIPPI SILT LOAM AS A PERCENT OF DOSE.

		COLUM		
COLUMN SECTION OR LEACHATE	#1	# 2	# 3	AVERAGE
1 Inch 2 3 4 5 6 7 8 9 10 11 12 TOTAL SOIL	67.18	47.24	60.86	58.43
	7.47	4.47	11.02	7.65
	4.78	2.87	6.01	4.55
	3.15	3.04	4.03	3.41
	2.75	3.70	3.08	3.18
	3.16	3.61	2.88	3.22
	3.16	2.84	2.51	2.84
	3.00	3.64	2.41	3.02
	2.63	2.58	1.77	2.33
	2.26	2.77	2.14	2.39
	1.91	2.60	1.48	1.99
	1.44	2.64	1.72	1.93
	102.89	82.01	99.92	94.94
LEACHATE	5.07	<u>9.13</u>	3.91	6.04
COLUMN TOTAL	107.96	91.14	103.83	100.98

TABLE 7: AVERAGE DISTRIBUTION PROFILE OF DIAZINON LEACHING IN FOUR SOIL TYPES PRESENTE AS PERCENT OF DOSED RADIOACTIVITY.

		SC	TYPE	
COLUMN SECTION OR LEACHATE	MARYLAND SAMD	CALIFORNIA SANDY LOAM	MARYLAND CLAY	MISSISSIPPI SILT LOAM
l inch 2 3 4 5 6 7 8 9 10 11 12 (bottom) COLUMN TOTAL	0.62 0.20 0.22 0.23 0.39 0.60 0.84 1.14 2.04 1.98 2.38 3.45	7.87 8.45 9.41 11.78 11.50 11.15 6.84 4.42 2.29 0.97 0.45 0.61 75.75	58.86 5.44 2.94 1.91 1.92 1.95 1.86 1.57 1.24 1.14 1.36 1.83 82.01	58.43 7.65 4.55 3.41 3.18 3.22 2.84 3.02 2.33 2.39 1.99 1.99 1.93
LEACHATE	81.25	17.55	<u>16.00</u>	6.04
TOTAL	95.34	93.30	98.01	100.98

TABLE 8: TLC CHARACTERIZATION OF THE COMBINED LEACHATES FROM SOIL COLUMNS. VALUES ARE AVERAGE PERCENT OF TLC SCANS FROM THREE REPLICATES CORRECTED TO PERCENT OF APPLIED DOSE.

SS: Toluene:Chloroform:Ethyl Alcohol:Formic Acid 8:9:2:1 v:v:v:v

	<u> </u>	<u>OXYPYRIMIDINE</u>	PARENT	REMAINDER
MD Sand	3.96	66.26	1.84	9.13
CA Sandy Loam	0.88	15.44	0.48	0.73
MS Silt Loam	0.20	5.28	0.12	0.44
MD Clay	0.15	44.63	0.27	0.94

SS: Hexane: Ethyl Acetate 8:2 v:v

	ORIGIN ^a	<u>OXYPYRIMIDINE</u>	PARENT	REMAINDER
MD Sand	-	71.82	2.84	6.52
CA Sandy Loam		15.54	0.71	1.29
MS Silt Loam	-	5.47	0.19	0.37
MD Clay	-	14.68	0.50	0.81

a) Oxypyrimidine remained at the origin in SS: hexane:ethyl acetate 8:2: v:v.

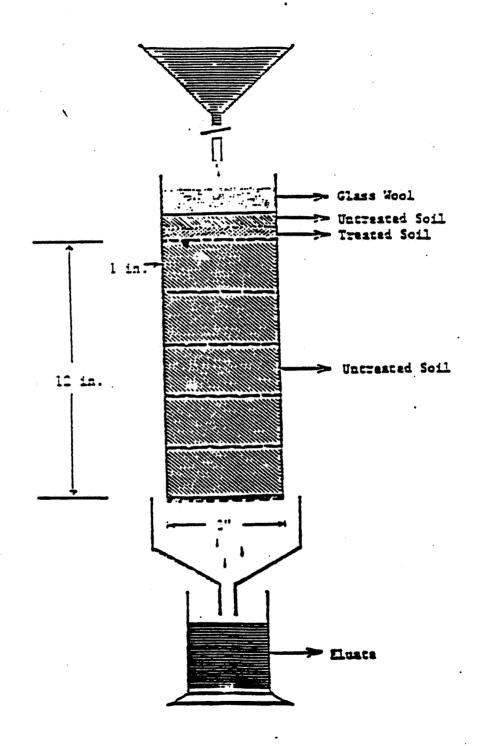
FIGURE 1: STRUCTURE OF DIAZIMON AND OXYPYRIMIDINE

$$\frac{\text{CH}_3}{\text{CH}_3} > \text{CH} \frac{\text{N}}{\text{N}} = \frac{\text{CH}_3}{\text{N}} = \frac{\text{OC}_2\text{H}_5}{\text{CC}_2\text{H}_5} = \frac{14\text{C}}{\text{C}_2\text{H}_5}$$

DIAZINON (G-24480)

OXYPYRIMIDINE (G-27550)

FIGURE 2. SOIL LEACHING COLUMN APPARATIS



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DISCUSSION:

- 1. The diazinon was well adsorbed to the top soil in each columns due to the fortification method used in this study. That was likely to decrease mobility.
- 2. Stability data on diazinon under the equilibrium and fortification conditions was not provided.
- 3. The source of the soils and/or soil series should be provided as background information.

24/

CASE GS238	DIAZINON		PM
CHEM 057801	Diazino		
BRANCH EAB	DISC	-	
FORMULATION 1	2 - EMULSIFIABLE	CONCENTRATE (EC), 09 - MICHOENCAPSULATED (MCAP)
FICHE/MASTER	ID 00118027, 001	20419	CONTENT CAT 01
Project Repor	t 02/79. Unpubl	ished study rece Switz., submitted	Basudin) under laboratory conditions: ived Nov. 5, 1982 under 4581-351; d by Agchem Div., Penrwalt Corp.,
Project Repor prepared by C	t 02/79. Unpubl	ished study rece Switz., submitted A.	Basudin) under laboratory conditions: ived Dec. 15, 1982 under 4581-335; d by Agchem Div., Pennwalt Corp.,
SUBST. CLASS	- S.	•	
DIRECT RVW TI	ME = 3 (MH)	START-DATE	
TITLE: ORG:	A. Abramovitch Chemist EPA 557-1975		•
	P. Mastradone Acting Chief EPA	•	DATE:
CONCLUSION:			

Degradation - Hydrolysis

The study was also evaluated in the EAB reviews of May 8, 1984 and Dec. 5, 1986 (EAB# 5794 & 4080).

This study is unacceptable because sterility and darkness was not maintained during the experiment. In addition, the identity and purity of the test substance was not specified. Also, a material balance was not provided, and degradates were not identified. This study would not fulfill EPA Hydrolysis Data Requirements for Registering Pesticides.

MATERIALS AND METHODS:

Buffer solutions were prepared in deionized water at:

pH 5 (0.1 M potassium hydrogen phathalate plus 0.05 M sodium hydroxide.

pH 7 (0.028 M potassium dihydrogen phosphate plus 0.041 M sodium hydrogen phosphate).

pH 9 (0.043 M borax plus 0.017 potassium dihydrogen phospate).

Diazinon standard (identity, purity, source unspecified) was added to each buffer solution. The concentration of diazinon in the buffers was not specified. The flasks were incubated at 30, 50 and 70°C. It was not specified whether samples were kept in the dark. Samples were taken at 0, 2, 4, 6, 8, 24, 32 and 48 days. Samples were extracted with methylene chloride and analyzed by GLC equipped with a flame photometric detector.

REPORTED RESULTS:

CALCULATED RATE CONSTANTS $(k_{\tt rate})$ AND HALF-LIVES $(t_{\tt 0.5})$ FOR DIAZZNON ASSUMBIG FIRST ORDER KINETICS UNDER THE DIFFERENT HYDROLYSIS CONDITIONS

hydrolysis medium	temperature °C	rate constant (k _{rate}) [s ⁻¹]	half-life (t _{0.5}) [h]	+,2
buffer pH 5	3 0	4.56 • 10-6	42	0.999
	50	1.46 • 10 ⁻⁵	13	0.998
	70	5.52 · 10 ⁻⁵	3.5	0.955
buffer pH 7	<i>3</i> 0	3.43 · 10 ⁻⁷	561	0.982
	50	2.55 · 10 ⁻⁶	76	0.998
	70	1.88 · 10 ⁻⁵	10	0.999
ouffer pH 9	3 0	6.84 · 10 ⁻⁷	282	0.999
	50	4.98 • 10 ⁻⁶	<i>3</i> 9	0.997
	70	3.75 · 10 ⁻⁵	5.1	0.998

hydrolysis period [h] [days]	၁,၀၄	20°C	70°C	υ ₀ ος	2 ₀ 02	2 ₀ 0L	ಶೃಜ	9 Hq	70,02
C	100	130	<u>8</u>	900	100	90	100	100	13
α:	1	ţ	£9	1	ı	82	j	i	3
4		83	44	ı	1	11	ı	ı	S
9	•	1	유	1	,•	63	3	,	R
€	•	59	8	1	1	55		, t	R
24 1	19	28	į	ı	81	19	. 1	92	-
32	. •	18	ı	1.	ì	12	1	ı	1
2 S4	\$	8	•	.j	02	#	•	64	'
ĸ	K	ı	*(53	•	ı	&	1
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	2	•	ı	30	អូ		£3	3	1

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- 7 55 5

DISCUSSION:

- 1. Sterility and darkness was not maintained during the experiment; therefore, degradation cannot be attributed solely to hydrolysis.
- 2. The purity of the test substance was not specified; pure active ingredient should be used.
- 3. No precautions were taken to minimize loss of the test substance by volatilization.
- 4. A material balance was not provided; and degradates were not identified.
- 5. The study was conducted at 30, 50 and 70°C and the results were extrapolated to 20°C.

CALCULATED RATE CONSTANTS ($k_{\tt pate}$) AND HALF-LIVES ($t_{\tt 0.5}$) FOR 20 $^{\circ}$ C USING THE ARRHENIUS PARAMETERS

	rate constants	half-life
	(k _{rate}) [s ⁻¹]	(t _{0.5}) [days]
buffer pH 5	2.09 • 10-6	3.8
buffer pH 7	$1.03 \cdot 10^{-7}$	78
buffer pH 9	2.03 · 10 ⁻⁷	40

EXECUTIVE SUMMARY

The data summarized below fulfill the photodegradation on soil, the aerobic, anaerobic and aquatic anaerobic soil metabolism. The <u>leaching</u> and <u>hydrolysis</u> data requirements are only partially fulfilled.

Diazinon degraded rapidly under aerobic, anaerobic, anaerobic aquatic and sterile soil conditions with the following half-lives:

31.2 days /aerobic 34.3 days /anaerobic 4.0 days/aquatic anaerobic* 46.0 days /sterile

* The faster aquatic anaerobic primary degradation of diazinon to oxypyrimidine than under anaerobic conditions might be attributed to hydrolysis under the acidic aqueous conditions at which the study was conducted.

Microbial degradation is an important pathway of degradation for diazinon; however, as seen from the half-lives under the various study systems, degradation continues in sterile and anaerobic systems which represent conditions of reduced microbial activity. The most probable mechanism responsible for degradation under these conditions in acidic soils appears to be chemical hydrolysis. Preliminary hydrolysis data indicate that diazinon is stable with respect to hydrolysis at pH 7 & 9 but hydrolyzes in non-sterile water of pH 5.

The major soil degradate is oxypyrimidine. Oxypyrimidine is more persistent than diazinon under aerobic, anaerobic and sterile conditions. Under anaerobic conditions, in which the parent compound (diazinon) was aged aerobically for 32 days before establishing anaerobic conditions, levels of oxypyrimidine did not increase above 21.2% of the original \$^{14}\$C dose at any time and decreased to 12.7% within 30 days. Oxypyrimidine reached a maximum concentration under aerobic soil condition in 95 days, accounting for 67% of the original \$^{14}\$C dose in the aerobic study system. Under aquatic anaerobic soil conditions, oxypyrimidine reached a maximum of 50% of the \$^{14}\$C dose at 9.2 days, and continued to increase reaching 54% of the \$^{14}\$C dose in 15 days. At the study's end (366 days), oxypyrimidine accounted for 55% of the original \$^{14}\$C dose.

A second degradate was identified as 2-(1'-hydroxy-1'-methyl)ethyl-4-methyl-6-hydroxypyrimidine, differing from oxypyrimidine only by an alcohol group. It reached a maximum concentration in 6 months time accounting for 12.8% of the original dose. Two unknown degradates were observed. They were not identified as they formed in amounts <1.0% of the original ¹⁴C dose in the aerobic and anaerobic study systems.

Incubated under strictly anaerobic conditions, exppyrimidine appears to accumulate and persist. Oxypyrimidine accounted for 55% of the 14 C dose at 366 days. The percentage of unextractable 14 C activity at 366 days was 45%. (DAS, 400287 & 401015-1).

Other supplementary aerobic soil metabolism data support the above findings. In a Swiss sardy loam soil at 75% of field capacity and 25°C, ring-labeled [14C]diazinon (97% pure) applied at 10 ppm, rapidly degraded to 2-isopropyl-4-methyl-6-hydroxypyrimidine (oxypyrimidine) with a half-life of less than one month (a half life of 11 days was reported by the study author, 23.7 days calculated by the reviewer, but additional data points are needed for a more

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accurate determination). Within 14 days only 12.3% of the activity was found as the parent; 72.9% was identified as exypyrimidine. Breakdown of exypyrimidine was slower than that of diazinon and 49% of the applied radioactive material was in the form of exypyrimidine after 84 days. After 166 days, the amount of exypyrimidine decreased to 4.7% of the applied material. Increased recoveries of $^{12}\text{CO}_2$ (55.6% after 166 days) and unextracted ^{14}C residues (15.1% after 166 days) corresponded to exypyrimidine breakdown. No other major metabolites were found. Radioactivity in the H_2SO_4 and ethylene glycol traps was <1% of the applied ^{14}C throughout the study and material balance was generally above 80% of the applied material (Keller, 00118031).

Approximately 81% of the applied unaged radioactive diazinon residues leached through a 30 cm Maryland sand column, 16% through a Maryland clay, 6% through a Mississippi silt loam and 17.5% through a California sandy loam soils with the application of 50.8 cm of water. In all cases, the predominent component in the leachate was oxypyrimidine, the primary degradate of diazinon. The parent diazinon was only present in the leachate in small amounts (Spare, 40512601).

The aged leaching data requirement remain unsatisfied but the following supplemental leaching data are available:

Aged residues of diazinon were observed in the leachate of a 30 cm sandy soil column of pii 7.8 when leached with 50.7 cm of water. About 32.7% of the applied material leached through the Collombey sand soil column and 25.3% through the sandy loam soil column. Most of the mobile material leached through with the initial application of less than 30 cm of irrigation. Oxypyrimidine, the primary degradate, was found in the leachate along with another degradate whose identity was not fully established. A second degradate was identified in the lacrobic soil metabolism data as 2-(1'-hydroxyl'-methyl)ethyl-4-methyl-6-hydroxypyrimidine, differing from oxypyrimidine only by an alcohol group. It was not identified in the aged residues leachate and the identity of the second degradate in the aged leachate should be confirmed in order to satisfy the aged soil column leaching data requirement (Buckhard, 00118034).

Aged residues of diazinon were observed in the leachate of a 30 cm sandy soil column of pH 7.8 when leached with 20.3 cm of water. Oxypyrimidine was the major degradate found in the leachate (Buckhard, 00132734-5).

Photodegradation of [14C]Diazinon (99% pure) at 7 or 51 ppm on sandy loam soil occurred with a half-life of 37.4 hours after exposure to natural light (Blair, 00153230). The degradate, oxypyrimidine, was detected at a maximum concentration of 19.60% (13.5 hours) of applied when exposed to natural sunlight. After 35.5 hours (37.4 hours is the half-life) of sunlight exposure, 20.7% of the radio-"labeled material was in soil bound residues (some of which contained ckypyrimidine), 24.4% was oxypyrimidine and 39.7% diazinon. Losses of 7% were attributed to volatilization of diazinon and degradates (of which 0.5% was carbon dioxide). The total [14C] radioactive material balance was 87-89% at the 0 hour and 84% at all other experimental points. In another study [14C]Diazinon (99% pure) degraded in sandy loam soil with a half-life of 17.3 hours when exposed to natural sunlight (Martinson, 00153229). The degradate, Oxypyrimidine, was detected at maximum concentrations of 23.72% (32.6 hours) of applied after exposure to natural sunlight. The degradate 2-(1'-hydroxy-1'-methyl)ethyl-4-methyl-6-hydroxypyrimidine was present after 8 hours of natural sunlight exposure at 3.6% of the applied material but was not present in the non-exposed samples. An unidentified degradate resulting from non-photolytic degradation (since it was also present in non-exposed

samples), accounted for about 7% of the applied under sunlight. The study gave a good account for the total amount of the applied radiolabeled material.

The <u>hydrolysis</u> data requirement remains unsatisfied since only acceptable data for pH 7 & 9 is available. At pH 7 & 9 diazinon is stable in water. At pH 5 diazinon hydrolyzed in <u>nonsterile</u> water and new data are needed under <u>sterile</u> conditions.

Environmental Fate Frofile.

The full potential of <u>Ground Water</u> contamination cannot be assessed without additional leaching and field dissipation data. However, the following observations with respect to ground water are made based on the available data:

<u>Diazinon</u> degraded under aerobic, anaerobic, anaerobic aquatic and sterile soil conditions with the half-lives of less than 46 days. Degradation occurred at a much faster rate on soil exposed to sunlight. Preliminary <u>hydrolysis</u> data indicate that diazinon is stable with respect to hydrolysis at pH 7 & 9 but hydrolyzes in non-sterile water of pH 5.

Oxypyrimidine is the primary degradate of diazinon in soil and it is also formed under photolysis and hydrolysis conditions. Oxypyrimidine is more persistent in soil than the parent diazinon and is more mobile than diazinon. Therefore, oxypyrimidine poses a larger potential to leach and contaminate ground water than diazinon Oxypyrimidine is mobile and is found in the leachate of sandy and sandy losm soil columns. A secondary degradate of oxypyrimidine was identified in the aerobic soil metabolism data as 2-(1'-hydroxy1'-methyl)ethyl-4-methyl-6-hydroxypyrimidine, differing from oxypyrimidine only by an alcohol group. Under anaerobic aquatic conditions these degradates are most likely to accumulate, persist and leach. The potential leaching of diazinon and its major degradates should be addressed by field dissipation studies to sufficient depths, using sensitive analytical methods to address the extent of leaching. The results of these studies might also trigger a small-scale prospective ground-water study to be conducted under conditions where leaching is observed.

RECOMMENDATIONS

Agricultural uses of diazinon do not appear to represent an unreasonable risk to humans. However, domestic use poisonings are a concern (see appendix). Also, there are ecological concerns associated with potential drift and run-off.

The submission of data relevant to reregistration requirements (Subdivision N) on terrestrial food crop, and nonfood crop, terrestrial noncrop, greenhouse food crop and nonfood crop, domestic indoor and outdoor, aquatic food crop, forestry, and indoor commercial and industrial sites are summarized as follows:

Hydrolysis studies: Two studies were reviewed. The first study (Agchem, 00118021) was only partially acceptable because sterility was not maintained during the experiment. The second study (Lichtenstein, 00120421) is unacceptable because sterility was not maintained during the study and would not fulfill data requirements because the analytical method used in the study (based on fly mortality) is unacceptable. In addition, the purity of the test substance was not specified, the test solutions were not buffered, the degradates were not quantified, the study was conducted for an insufficient length of time, the amount of co-solvent (acetone) was unspecified and a material balance was not provided. Hydrolysis data at pH 5 in sterile conditions are needed.

Photodegradation studies in water: One study (Martinson, 00153231) was reviewed and is unacceptable because sunlight conditions were not simulated. All data are required.

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Photodegradation studies on soil: Two studies were submitted (Blair, 00153230, and Martinson, 00153229) and the portions of the studies involving irradiation with natural sunlight satisfy this data requirement.

Photodegradation studies in air: No data were submitted; however, the data requirement is deferred pending toxicology and reentry concerns.

Aerobic soil metabolism studies: Several studies were reviewed. One study (DAS, 400287) satisfy the data requirement. Another study (Keller, 00118031) that was conducted on a Swiss soil can also satisfy this data requirement provided that similar results are obtained in field dissipation studies on US soils and accurate half life values for the initial degradation of diazinon are provided. Another study (Getzin and Rosefield, 00011825) only provides supplemental data because degradates were not identified, and the test substance was not technical grade or purer. The fourth study (Miles et al, 00073059) also provides supplemental data but material balance was not provided, the purity of the test substance was unspecified, the patterns of formation and decline of degradation products were not addressed, and the soils were not completely characterized. The fifth study (Lichtenstein, 00120421) is unacceptable because the sampling interval (one sample) was inadequate, and the method was not described in sufficient detail to adequately assess the degradation of the test substance in soil. In addition, this study would not fulfill data requirements because the soil was incompletely characterized, the test substance was uncharacterized, degradates were not identified, a material balance was not provided, and the incubation temperature was not reported (Experiment 1). The last study reviewed (Harris, 00095199) is unacceptable because the experimental procedures were inadequate to assess the degradation of diazinon in soil, a non-specific bioassay was the only analytical procedure employed, the pattern of formation and decline of degradates was not addressed, and the soil moisture varied between 50 and 100% of field capacity. The aerobic soil metabolism data requirement is satisfied and no additional data are required.

Anaerobic soil metabolism studies: One study (Das. 400287) satisfies the data requirement.

Anaerobic aquatic metabolism studies: One study (Das, 401015 satisfies data requirments.

Aerobic aquatic metabolism studies: No data were submitted, but data are required.

Leaching and adsorption/desorption studies: Several studies were reviewed. The unaged leaching data requirement is satisfied (Spare, 40512601). Supplemental unaged adsorption/desorption data (Guth & Imhof, 00118032). The study can be fully accepted if satisfactory answers are provided to questions raised in Task 1, study 24. The aged soil column leaching study (Buckhard, 00118034) can satisfy the aged soil leaching data requirement provided that the identity of the second degradate present in the leachate is confirmed. Until provided, the aged soil leaching data requirement remain unsatisfied.

Supplemental data is provided by several studies: The study (Agchem, 00118022, 00118023) were found defficient because the columns were leached with an insufficient volume of water (15.7 inches), the analytical method was not described in sufficient detail to adequately assess the mobility of the test substance in soil and the test substance was not of sufficient purity. (Agchem, 00118023) was found defficient because the test substance was not of sufficient purity.

(Ciba-Geigy Corp., 00053135) could not be accepted because the soil columns were leached with an insufficient amount of water (7.87 inches), the analytical method was not described and the test substance was not technical grade or purer.

The study (Harris, 00122690) is unacceptable because subirrigated soil columns do not measure downward mobility, the purity of the test substance was not reported, the test soils were not completely characterized and the amount of water absorbed by the column was not reported. .

Laboratory volatility studies: No data were submitted; however, the requirement is deferred pending toxicology and reentry concerns.

Field volatility studies: No data were submitted: however, the data requirement is deferred pending the receipt of acceptable laboratory volatility data.

Terrestrial field dissipation studies: Five studies were reviewed. The portion of the study (Agchem, 00118024) pertaining to the California loam, the Washington sandy loam and the Pennsylvania silty loam soils is soil provide supplemental information but do not fulfill data requirements because the test substance was uncharacterized, complete field test data were not reported, and the patterns of formation and decline of degradates were not addressed. The portion of the study pertaining to the Texas loam is unacceptable because the sampling interval is inadequate to assess the dissipation of diazinon in soil. The second study (Getzin and Rosefield, 00011825) provides supplemental information but does not fulfill data requirements because the purity of the test substance was unspecified, pretreatment samples were not taken, degradates were not identified, complete field test data were not reported, and the material balance was insufficient. The third study (Burkhardt and Fairchild, 00092960) is unacceptable because a nonspecific bioassay was used for analysis. The fourth study (Kadoum et al, 00103643) is unacceptable because the analytical method was not described and the sampling intervals were inadequate to accurately assess the dissipation of the test substance from soil, the test substance and soil were uncharacterized, complete field test data were not reported, and degradates were not characterized. The fifth study (Rusk et al. 00092604) could not be accepted because the analytical method was not described in sufficient detail to properly assess the dissipation of the test substance from soil, the test soil was not completely characterized, meteorological data was not provided, the use in soil confined in 55-gallon drums may not be representative of dissipation under actual field conditions, and vertical movement of residues was not addressed. In general, none of the field studies was conducted to sufficient depths and under conditions exemplifying worse leaching leaching conditions under actual agricutural uses. The potential leaching of diazinon and its two degradates should be addressed by field dissipation studies to sufficient depths, using sensitive analytical methods to address the extent of leaching. The results of these studies might also trigger a small-scale prospective ground-water study to be conducted under conditions where leaching is observed.

Aquatic field dissipation studies: No data were submitted but data are required.

Forestry dissipation studies: No data were submitted, but all data are required.

Long-term field dissipation studies: No data were submitted; however, the data requirement is deferred pending the receipt of acceptable terrestrial field dissipation data.

Confined accumulation studies on rotational crops: No data were submitted, but all data are required. 522

Field accumulation studies on rotational crops: No data were submitted; however, the data requirement is deferred pending the receipt of acceptable confined rotational crop accumulation data.

Accumulation studies on irrigated crops: No data were submitted, but all data are required.

Laboratory studies of pesticide accumulation in fish: No data were submitted, but all data are required.

Field accumulation studies on aquatic nontarget organisms: No data were submitted; however, the data requirement is deferred pending the receipt of acceptable laboratory fish accumulation data, field and aquatic dissipation data and concerns of the Ecological Effects Branch/HED.

Reentry studies: One study (Skinner and Kilgore, 00153973) was reviewed but it did not provide useful data for the estimation of fieldworker exposure to residues of diazinon nor the calculation of a reentry interval. All data are required.

Spray Drift studies: No studies were reviewed but data are required.

Run-off study: One study (Ritter et al., 00027142) on the mobility of diazinon in the runoff from diazinon-treated plots was reviewed and is scientifically valid.

REFERENCES

The following studies were reviewed in Task I:

Agchem. 1979. Adsorption and desorption of Knox Out 2FM versus diazinon E.C. in soils: Project No. WT-6-78. Unpublished study received Nov. 5, 1982 under 4581-351; CDL:248818-D. (00118023)

Agchem. 1979. Knox Out 2FM and diazinon E.C.-soil leaching: Project No. WT-2-78 Unpublished study received Nov. 5, 1982 under 4581-351; CDL:248818-C. (00118022)

Agchem. 1981. Knox Out 2FM insecticide--field dissipation: Project No. WT-5-81. Unpublished study received Nov. 5, 1982 under 4581-351; CDL:248818-E. (00118024)

Agchem. 1982. Hydrolysis study--Knox Out 2FM Insecticide versus Diazinon E.C.: Project No. WT-4-79. Unpublished study received Nov. 5, 1982 under 4581-351; CDL:248818-B. (00118021)

Blair, J. 1985. Photodegradation of diazinon on soil: Study No. 6015-208. Unpublished study prepared by Hazleton Laboratories America, Inc. (00153230)

Buckhard, N. 1979. Hydrolysis of diazinon (Basudin) under laboratory conditions: Project Report 02/79. Unpublished study received Nov. 5, 1982 under 4581-351; prepared by Ciba-Geigy Ltd., Switz., submitted by Agchem Div., Pennwalt Corp., Philadelphia, PA; CDL:2348818-H. (00118027)

Buckhard, N. 1979. Hydrolysis of diazinon (Basudin) under laboratory conditions: Project Report 02/79. Unpublished study received Dec. 15, 1982 under 4581-335; prepared by Ciba-Geigy Ltd., Switz., submitted by Agchem Div., Pennwalt Corp., Philadelphia, PA; CDL:249074-A. (00120419)

Burkhardt, C.C., and M.L. Fairchild. 1967. Bioassay of field-treated soils

- to determine bioactivity and movement of insecticides. J. of Econ. Entomol. 60(6):1602-1610. Also In unpublished submission received Sept. 8, 1970 under unknown admin. no.; submitted by American Cyanamid Co., Princeton, NJ; CDL:120350-C. (00092960)
- Buckhard, N. 1980. Leaching characteristics of aged ¹⁴C-diazinon (Basudin) residues in two standard soils: Project Report 09/80. Unpublished study received Nov. 5, 1982 under 4581-351; prepared by Ciba-Geigy Ltd., Switz., submitted by Agchem, Pennwalt Corp., Philadelphia, PA; CDL:248818-0. (00118034)
- Buckhard, N., T. Winkler, and K. Ræmsteiner. 1980. Leaching characteristics of aged ¹⁴C-diazinon (Basudin) residues in two standard soils: Project Report 09/80. Unpublished study received Nov. 17, 1983 under 100-469; prepared by Ciba-Geigy Ltd., Switz., submitted by Ciba-Geigy Corp., Greensboro, NC; CDL:251777-P. (00132735)
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- Ciba-Geigy Corporation. 1974. The influence of soil humidity, amount and intensity of rainfall on the leaching behavior of pesticides: No. SPR 44/74. Unpublished study received Oct. 8, 1976 under 7G1877; CDL: 095322-G. (00053135)
- Getzin, L.W. and I. Rosefield. 1966. Persistence of diazinon and zinophos in soils. J. of Econ. Entomo. 59(3):512-516. Also <u>In unpublished submission received May 12, 1972 under 100-501; submitted by Ciba-Geigy Corp.</u>, Greensboro, NC: CDL:120412-E. (00011825)
- Guth, J. 1972. Adsorption and leaching behaviour of diazinon in various soils: SPR 46/72 S. Unpublished study received Nov. 5, 1982 under 4581-351; prepared by Ciba-Geigy Ltd., Switz., submitted by Agchem Div., Pennwalt Corp., Philadelphia, PA; CDL:248818-M. (00118032)
- Harris, C.R. 1969. Laboratory studies on the persistence of biological activity of some insecticides in soils. J. Econ. Entomol. 62(6):1437-1441. Also In unpublished submission received Aug. 28, 1972 under 3F1306; submitted by Dow Chemical Co., Indianapolis, IN; CDL:092219-G. (00095199)
- Harris, C. 1969. Movement of pesticide in soil. J. Agr. Food Chem. 17(1). Also In unpublished submission received Nov. 19, 1982 under HI 79/2; submitted by Velsicol Chemical Corp., Chicago, IL; CDL:248932-D. (00122690)
- Kadoum, A., T. Hopkins, and H. Knutson. 1969. Reduction of hazards associated with the presence of residues of insecticidal chemicals in the environment: NC-85. Progress rept., Oct. 16, 1969. Unpublished study
- Keller, A. 1981. Degradation of Basudin in aerobic soil: Project Report 37/81. Accession No. 251777. Report 7. Unpublished study received Nov. 5, 1982 under 4581-351; prepared by Ciba-Geigy, Ltd., Switz., submitted by Agchem Div., Pennwalt Corp., Philadelphia, PA; CDL:248818-L. (00118031)
- received on unknown date under 9F0786; prepared by Kansas State Univ., Agricultural Experiment Station, Dept. of Entomol., submitted by Shell Chemical Co., Washington, DC; CDL:095474-F. (00103643)

Lichtenstein, E., T. Fuhremann, and K. Schulz. 1968. Effect of sterilizing agents on persistence of parathion and diazinon in soils and water. J. Agric. Food Chem. 16(5):870-873. Also In unpublished submission received Dec. 15, 1982 under 4581-335; submitted by Agchem Div., Pennwalt Corp., Philadelphia, PA; CDL:249074-Q. (00120421)

Martinson, J. 1985. Photodegradation of [carbon-14]-diazinon in water: Final Report: Biospherics Project No. 85-E-044 PW. Unpublished study prepared by Biospherics Inc. 90 p. (00153231)

Martinson, J. 1985. Photolysis of diazinon on soil: Final Report Biospherics Project No. 85-E-044 SP. Unpublished study prepared by Biospherics Inc. 135 p. (00153229)

Miles, J.R.W., C.M. Tu, and C.R. Harris. 1979. Persistence of eight organophosporus insecticides in sterile and nonsterile mineral and organic soils. Bull. of Environ. Contam. and Toxicol. 22:312-318. Also In unpublished submission received June 27, 1979 under 464-448; submitted by Dow Chemical U.S.A., Midland, MI; CDL:238974-A. (00073059)

Ritter, W.F., H.P. Johnson, and W.G. Lovely, et al. 1974. Atrazine, propachlor, and diazinon residues on small agricultural watersheds: Runoff losses, persistence, and movement. Environ. Sci. and Technol. 8(1):38-42. Also In unpublished submission received July 19, 1978 under 201-403; submitted by Shell Chemical Co., Washington, D.C.; CDL:234472-T. (00027142)

Rusk, H.W., S. Esvelt, and B.J. Landis. 1965. Report of residue analysis: Report No. PCY-65-30. U.S. Agricultural Research Service, Entomology Research Div., Pesticide Chemicals Research Branch, Potato, Pea and Sugar Beet Insects Investigations; unpublished study; CDL:091231-B. (00092604)

Skinner, C., and W. Kilgore. 1982. Application of a dermal self-exposure model to worker reentry. J. Toxicol. Environ. Health 9(3):461-481. (00153973)

Spare, W., 1987. Leaching characteristics of diazinon. Unpublished study received Feb. 23, 1988. Prepared by and submitted by Ciba-Geigy Corporation. (40512601).

The following studies were not reviewed because they do not contain diazinon data:

Riley, D. and J.E. Stevens. 1975. Pirimiphos-ethyl: Leaching in soil: AR 2592A. Unpublished study received Dec. 17, 1976 under 10182-9; prepared by Plant Protection Ltd., submitted by ICI Americas, Inc., Wilmington, DE; CDL:227314-W. (00068104)

Ritter, W.F. 1971. Environmental factors affecting the movement of atrazine, propachlor and diazinon in Ida silt loam. Doctoral dissertation, Iowa State Univ. Unpublished study received Oct. 19, 1972 under 279-2712; prepared by Iowa State Univ., Depts. of Agricultural Engineering and Civil Engineering, submitted by FMC Corp., Philadelphia, PA; CDL:094077-AB). (00040372)

The following studies were not reviewed because they do not contain environmental fate data:

Laygo, E.R., and J.T. Schulz. 1963. Persistence of organophosphate insecticides and their effects on microfauna in soils. Ann. Proc., North Dakota Academy of Science 17:64-65. Abstract; also In unpublished submission received Sept. 8, 1970 under unknown admin. no.; submitted by American Cyanamid Co., Princeton, NJ; CDL:120350-AA. (00092975)
Ritter, W.F., H.P. Johnson, and W.G. Lovely. 1973. Diffusion of atrazine, propachlor, and diazinon in a silt loam soil. Weed Sci. 21(5):381-384.
Also In unpublished submission received July 19, 1978 under 201-403; submitted by Shell Chemical Co., Washington, D.C.; CDL:234472-H. (00027133)

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Kaufman, D.D., and D.E. Miller. 1970. Controlled biodegradation and persistence of several amide, carbamate, and urea herbicides. In Abstracts from the 1970 Meeting of the Weed Science Society of America. N.P. Also In unpublished submission received on unknown date under 4F1429; submitted by Pittsburgh Plate Glass Co., Morristown, NJ; CDL:093807-D. (00037019)

The following studies were not reviewed because they contain product chemistry data only:

Ciba-Geigy Corp. 1974. Chemistry of Basudin 401. Compilation; unpublished study received Nov. 17, 1983 under 100-469; CDL:251777-M. (00132732)

Gysin, H. 1956. Name, chemical identity and composition of diazinon. Unpublished study received Nov. 2, 1956 under PP0110; submitted by Ciba-Geigy Corp., Greensboro, NC; CDL:094753-A. (00124006)

The following study was not reviewed because it contains exposure data only:

Freeborg, R., W. Daniel, and V. Konopinski. 1985. Applicator exposure to pesticides applied to turfgrass. P. 287-295 in unknown source. American Chemical Society. (00148438)

The following study was not reviewed because it contains treated crop residue data only:

Braun, H., G. Ritcey, and R. Frank, et al. 1980. Dissipation rates of insecticides in six minor vegetable crops grown on organic soils in Ontario, Canada. Pest. Sci. 11(6):605-616. (00154019)

The following studies were not reviewed because they are duplicates of:

00122690

Harris, C.H. 1969. Movement of pesticides in soil. J. of Agric. and Food Chem. 17(1):80-82. Also <u>In</u> unpublished submission received Oct. 19, 1972 under 279-2712; submitted by FMC Corp., Philadelphia, PA; CDL:094077-T. (00040364)

Harris, C.I. 1969. Movement of pesticide in soil. J. of Food and Agric. Chem. 17(?):80-82. Also <u>In</u> unpublished submission received Nov. 3, 1971 under 0F0957; submitted by Union Carbide Agricultural Products Co., Ambler, PA: CDL:095875-S. (00039346)



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- Lichtenstein, E., T. Fuhremann, and K. Schulz. 1968. Effect of sterilizing agents on persistence of parathion and diazinon in soils and water. J. Agric. Food Chem. 16(5):870-873. Also In unpublished submission received Dec. 15, 1982 under 4581-335; submitted by Agchem Div., Pennwalt Corp., Philadelphia, PA; CDL:249074-Q. (00120421)
 - The following studies were not reviewed because they were previously reviewed in EAB Review of May 8, 1984 (see Appendix):
 - Buckhard, N. 1978. Photolysis of diazinon (Basudin) on soil surfaces under artificial sunlight conditions: Project Report 2/78. Unpublished study prepared by Ciba-Geigy Ltd. 16 p. (00146733)
 - Buckhard, N. 1979. Photolysis of diazinon (Basudin) under laboratory conditions: Project Report 02/79. Unpublished study received Nov. 17, 1983 under 100-469; prepared by Ciba-Geigy Ltd., Switz., submitted by Ciba-Geigy Corp., Greensboro, NC; CDL:251777-A. (00132724)
 - Cowart, R., F. Bonner, and E. Epps. 1971. Rate of hydrolysis of seven organophosphate pesticides. Bull. Environ. Contamin. Toxicol. 6(3): 231-234. Also In unpublished submission received Nov. 17, 1983 under 100-469; submitted by Ciba-Geigy Corp., Greensboro, NC; CDL:251777-B. (00132725)
- Frank, J., K. Balu, and A. Hofberg. 1972. Photolysis of diazinon in aqueous solution under natural and artificial sunlight conditions: Report No. GAAC-72115. Unpublished study received Nov. 17, 1983 under 100-469; submitted by Ciba-Geigy Corp., Greensboro, NC; CDL:251777-E. (00132728)
- Getzin, L. 1967. Metabolism of diazinon and zinophos in soils. J. Econ. Entomol. 60(8):505-508. Also In unpublished submission received Nov. 17, 1983 under 100-469; submitted by Ciba-Geigy Corp., Greensboro, NC; CDL:251777-J. (00132730)
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APPENDIX