

US EPA ARCHIVE DOCUMENT

#041701

DYNAMAC
CORPORATION

041701

FONOFOS

Task 1: Review and Evaluation of Individual Studies

Contract No. 68-01-6679

Final Report

February 24, 1983

Submitted to:

Environmental Protection Agency
Arlington, Virginia 22202

Submitted by:

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Enviro Control Division
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FONOFOS

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- 9 Ahmed, N., and F.O. Marrison. 1972. Longevity of residues of four organophosphate insecticides in soil.
- 10 Kiigemagi, U., and L.C. Terriere. 1971. The persistence of Zinophos and Dyfonate in soil.
- 11 Schulz, K.R., and E.P. Lichtenstein. 1971. Field studies on the persistence and movement of Dyfonate in soil.
- 12 Talekar, N.S., L.T. Sun, E.M. Lee, and J.S. Chen. 1977. Persistence of some insecticides in subtropical soil.
- 13 Lichtenstein, E.P., H. Parlar, F. Korte, and A. Suss. 1977. Identification of [¹⁴C]fonofos metabolites isolated from insecticide-treated culture media of the soil fungus Rhizopus japonicus.

14

Bionomics, Inc. 1972. Exposure of fish to labeled Dyfonate, accumulation, distribution and elimination of residues.

CASE GS 0105 FONOPOS STUDY 1 PM 300 07/15/82

CHEM 041701 Fonofos

BRANCH EFB DISC 30 TOPIC 050530 GUIDELINE 40 CFR 163.62-10b

FORMULATION 04 - GRANULAR

FICHE/MASTER ID 00090831 CONTENT CAT 01

McBain, J.B., and J.J. Menn. 1966? Persistence of O-Ethyl-s-phenyl ethylphosphonodithioate (Dyfonate) in soils: ARC-B-10. Unpublished study received Nov. 1, 1971 under OF0960 submitted by Stauffer Chemical Co., Richmond, Calif.; CDL:094505-J.

SUBST. CLASS = S.

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

REVIEWED BY: W. Spangler
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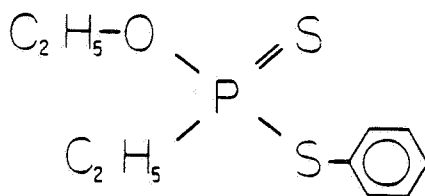
CONCLUSIONS:

Metabolism - Aerobic Soil

1. This study is scientifically valid.
2. Fonofos was degraded at a moderate rate with half-lives ranging from 11 weeks to >16 weeks. The degradation rate showed no definite correlation to temperature, soil moisture, pH, organic matter, or CEC. No major metabolite was identified.
3. This study does not fulfill EPA Data Requirements for Registering Pesticides (1983) because a formulated product was used.

MATERIALS AND METHODS:

FONOFOS, DYFONATE, N-2788



O-Ethyl-S-phenylethylphosphonodithioate

Felton loamy sand, Sorrento clay loam, Bowers clay loam, and Delta peat soils (Table 1) were collected from the field, sieved to ≤ 1 mm, and dried at 110 C. Fonofos (5% G, Stauffer Chemical Co.) was added to the soils at 10 ppm. The soils were mixed, the moisture level adjusted within the range of 20% of field capacity to saturation, and placed in pint jars with 1-1.5 inches of airspace. Sixteen sterile control samples were prepared for each soil by autoclaving three times at 15 pounds for 2 hours at 2-day intervals. The soils were autoclaved a fourth time, 1 week later, and fonofos was added under aseptic conditions. All nonsterile samples were incubated aerobically in the dark at 4.4 and 23.9 C. Sterile samples were incubated at 23.9 C only.

Samples were removed periodically, moisture was determined, and 100 g (dry weight equivalent) was extracted by blending with acetone. The surry was vacuum filtered, homogenized a second time with acetone, and the combined extracts dried over anhydrous sodium sulfate. Dry extracts were evaporated to dryness, reconstituted in benzene, dried over sodium sulfate, and analyzed for fonofos residues by using GLC with a phosphorus detector. The linear response range was 0.5 to 1.5 ng fonofos. The oxygen analog (dyfoxon) had the same retention time as fonofos but the detector response was much less, therefore, dyfoxon was analyzed for by an anticholinesterase assay, using human serum, described by Michel (1949. J. Lab. Clin. Med. 3(11):1564-1568).

REPORTED RESULTS:

Fonofos was degraded at a moderate rate in soils with half-lives ranging from 11 weeks in sterile or nonsterile Sorrento clay loam at 23.9 C to much greater than 16 weeks in nonsterile Bowers clay loam at 23.9 C. For the four soils the half lives of fonofos decreased in the following order: Bowers clay loam 1 = Delta peat > Sorrento clay loam > Felton loamy sand (Table 2). Microorganisms did not appear to contribute significantly to fonofos degradation; in fact, the half-lives were generally shorter in the absence of microorganisms. Sterility was not maintained, however, throughout the course of the experiment. Hydrolysis appeared to be the major route of degradation although the rate of degradation was not affected significantly by moisture level. Similarly, the degradation rate showed no definite correlation to temperature, pH, organic matter, or CEC. Only traces of dyfoxon were detected in 2-4 months.

DISCUSSION:

No major metabolite was detected in this study. Sterility was lost in controls during the course of the investigation, presumably due to adding nonsterile fonofos to sterile soil.

Table 1. Soil characteristics.

Soil	Mechanical analysis			pH	Organic matter (%)	CEC (meq/100 g)	Moisture saturation (%)
	Sand	Silt (%)	Clay				
Felton sandy loam	93.2	3.5	1.6	5.0	1.7	6.2	14
Sorrento clay loam	37.0	38.5	18.9	6.9	5.6	23.9	2.6
Bowers clay loam	30.2	28.8	29.4	7.1	11.6	52.2	35
Delta peat	40.5	12.6	11.3	4.7	34.6	51.5	45

Table 2. Half-life determinations for fonofos in four soils.

Soil	Temperature (C)	Sterile	Moisture (%)	Half-life (weeks)	Fonofos remaining after 16 weeks (%)
Felton loamy sand	23.9	yes	8.7	12	47
	23.9	no	8.5	13	47
	23.9	no	1.9	12	35
	4.4	no	8.6	16	35
	4.4	no	1.8	12	35
Sorrento clay loam	23.9	yes	12.2	11	44
	23.9	no	12.9	>16	66
	23.9	no	2.9	11	34
	4.4	no	12.2	12	35
	4.4	no	2.9	>16	92
Bowers clay loam	23.9	yes	16.6	16	52
	23.9	no	19.1	>16	76
	23.9	no	6.1	>16	100
	4.4	no	19.0	>16	71
	4.4	no	6.3	>16	71
Delta peat	23.9	no	36.5	>16	58
	4.4	no	36.1	>16	55

CASE GS 0105 FONOFOS STUDY 2 PM 300 07/15/82

CHEM 041701 Fonofos

BRANCH EFB DISC 30 TOPIC 050520

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID 00052058 CONTENT CAT 01

Hoffman, L.J., J.B. McBain, and J.J. Menn. 1973. Environmental behavior of O-ethyl S-phenyl ethylphosphonodithioate (Dyfonate): ARC-B-35. Unpublished study received April 2, 1973 under 6FL379; submitted by Stauffer Chemical Co., Richmond, Calif.; CDL:093686-B.

SUBST. CLASS = S. OTHER SUBJECT DESCRIPTORS PRIM: RCBR-20-150505 SEC: EFB -30-05052005 EFB-30-05101505 EFB -30-050525 RCBR-20-1515 EFB -20-1015

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

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CONCLUSIONS:

Metabolism - Aerobic Soil

- 1. This portion of the study is scientifically valid.
2. Fonofos was degraded in a loamy sand soil with a half-life of ~3 months. As organoextractable residues decreased with time, the percentage of unrecoverable activity increased. After 24 months, 50% of the initial radioactivity was unrecoverable. The major water soluble degradate (8% of initial activity) was O-ethylethane phosphonothioic acid.
2. This portion of the study partially fulfills EPA Data Requirements for Registering Pesticides (1983) by identifying degradates of fonofos incubated in a loamy sand soil

Degradation - Photodegradation in Water

This portion of the study is scientifically invalid because photolysis was studied in nonsterile tap water.

Combined supernatants were further extracted twice with dichloromethane to give aqueous and organosoluble fractions. The radioactivity was quantified, fractions were concentrated by vacuum evaporation, and aliquots were cochromatographed with authentic reference standards by using TLC on silica gel plates. Radiolabeled spots were located by using autoradiography, scraped from the plates, and quantified by using LSC. Non radiolabeled standards were detected with iodine vapors or by UV fluorescence quenching.

Degradation - Photodegradation in Water

Phenyl-labeled and 1-ethoxy-labeled [^{14}C]fonofos (0.8 and 0.9 mCi/mM, respectively) were dissolved in acetone and added at 12 ppm to tap water at pH 7. Portions (10 ml) were pipetted into glass Petri dishes and exposed directly to sunlight or covered with aluminum foil and kept as dark controls. Exposure was to July sunlight in the Santa Clara Valley, California with exposure from 0900-1700 hours at a light intensity of 8000 foot candles (at noon). Evaporation losses were corrected and a volatility control was maintained frozen. Periodic samples were extracted with dichloromethane, assayed for total radioactivity by using LSC, concentrated, and residues separated by using silica gel cochromatography with a chloroform:ethyl acetate (1:1, v:v) solvent mixture. Spots were located and quantified as described above.

Degradation - Photodegradation on Soil

Sorrento loam soil (36% sand, 39% silt, 25% clay, 5.5% organic matter, pH 6.3, 12% moisture, and CEC 29.8 meq/100 g) was sieved to ≤ 2 mm and slurried with 10.6 ppm solution of phenyl-labeled [^{14}C]fonofos (specific activity 2.9 mCi/mM) and exposed to sunlight at 8000 foot candle intensity (noon) for 8-hour periods (0800-1600 hours). Dark controls were included as well as dark and light sterile controls (autoclaved 1 hour at 120 C prior to being treated). After 12, 28, and 68 hours of exposure, samples were extracted four times with water:acetone:methanol, 1:1:1), centrifuged, and apolar products were extracted from supernatants by extracting five times with dichloromethane. Radioactivity in soils (combusted) and extracts was quantified and extracts (apolar metabolites) were separated by using two-dimensional TLC and quantified by using LSC.

Mobility - Leaching

Leaching of fonofos by runoff water was studied in an inclined plane with a 15° slope. The tray was filled with Sorrento loam soil and 2.0×10^8 dpm of 1-ethoxy-labeled or phenyl-labeled [^{14}C]fonofos was added to the upper 1 foot of the 3-foot inclined plane and mixed to a depth of 0.5 inches. Duplicate plots were treated for each label and plots were placed outdoors in an open field for 1 month (August). Each day, 0.1 inches of water was slowly sprinkled over the surface in two applications and after 30 days a 0.2-inch drench was applied in 5 minutes resulting in runoff but no significant erosion. The runoff was collected and soil cores taken from six locations in each inclined plane. The silt from the runoff was extracted with methanol:water (1:1, v:v) as described for soil metabolism studies. Extracted silt and aliquots of

upper and lower core halves were combusted and radioactivity quantified by using LSC. Runoff water and silt extracts were combined, radioassayed by using LSC and extracted twice with dichloromethane. Aqueous and organosoluble fractions were assayed for radioactivity and degradates were separated and identified by using TLC.

Confined Accumulation - Rotational Crops

Soils which had been aged for 3-24 months in the aerobic metabolism study, containing only bound ^{14}C residues, were air-dried, mixed with four parts of untreated Felton sandy loam, and placed in aluminum trays. Each tray was planted with 10 barley and 10 soybean seeds at 21-27 C and watered as necessary. Single seedlings of each species were removed (whole) at 4, 6, 12, 21, and 34 days after planting, soil debris was removed and the plants were combusted to $^{14}\text{CO}_2$ and water and radioassayed by using LSC. Residual activity was measured in the soil and the amount of activity available per plant was determined. This amount was compared to actual uptake.

REPORTED RESULTS:

Metabolism - Aerobic Soil

Fonofos disappeared fairly rapidly from Felton loamy sand with a half-life of ~ 3 months. The half-life of the organosoluble fraction was ~ 5.5 months for 1-ethoxy-labeled [^{14}C]fonofos and ~ 3 months for phenyl-labeled [^{14}C]fonofos. At each sampling period, the percentage of unrecoverable activity increased to a final value of $\sim 50\%$ for either label after 24 months. There was a concomitant decrease in organosoluble fractions with time. The major water soluble degradate detected was O-ethylethane phosphonothioic acid (Table 1).

Degradation - Photodegradation in Water

The decay patterns for 1-ethoxy-labeled and phenyl-labeled [^{14}C]fonofos were identical with sunlight and darkness (half-lives of 2 and 8 hours, respectively). The principal apolar component recovered was fonofos with no major degradates found. As organosoluble radioactivity decreased, water soluble activity did not concomitantly increase beyond the initial level indicating that neither photolytic nor hydrolytic mechanisms account for losses of fonofos from water. It appeared that losses occurred by codistillation with water (evaporation).

Degradation - Photodegradation on Soil

The results of photolysis in soil slurries were very similar to those in aqueous solutions, no gross difference was observed for autoclaved versus non-autoclaved soils. Organosoluble ^{14}C activity dissipated rapidly and was more pronounced in the sunlight than in the dark. No major metabolites were detected and only traces of methyl phenyl sulfoxide and methyl phenyl sulfone were found. These apparently were formed by soil microorganisms because very little of either was found in autoclaved samples, and none was observed in frozen controls.

Parent compound was the major product in the organosoluble fraction, and its activity was lost at a rate much greater than the buildup of water soluble compounds. After 12 days, 97% of the original activity in a frozen control was recovered as parent compound. Fonofos is apparently lost from soil slurries, primarily by volatilization rather than by photolysis or hydrolysis.

Mobility - Leaching

Runoff collected after drenching Sorrento loam soil, which had aged 30 days, was collected as 615-700 ml of water containing 51-140 g of silt. Of the applied radioactivity, 0.54 and 1.2% were collected in the runoff from soils treated with 1-ethoxy-labeled and phenyl-labeled [^{14}C]fonofos, respectively. Of the total 1-ethoxy-labeled [^{14}C]fonofos activity recovered, 43% was associated with the silt, 45% was organo-extractable, and 12% was found in the aqueous fraction. Parent compound accounted for 92% of the organosoluble fraction for the phenyl-labeled [^{14}C]fonofos runoff, 62% of the activity was associated with the silt, while 26 and 12% was present as organosoluble and aqueous radioactivity. The major product in the organosoluble fraction was fonofos (49%), with some diphenyl disulfide (29%), and a small amount of apolar products (3%). Radioactivity in cores from the 1-ethoxy-labeled [^{14}C]fonofos treated plot accounted for 1.8 ppm in the upper 6 inches of the application site, and 0.2 ppm in the lower 6 inches. The respective recoveries for the phenyl-labeled [^{14}C]fonofos treated plots were 2.0 (upper) and 0.05 ppm (lower).

Confined Accumulation - Rotational Crops

Barley and soybean plants grown in soil containing non-extractable ^{14}C residues of fonofos generally exhibited low uptake and translocation of radioactivity with no correlation to the length of time the soil was aged prior to planting. One exception was the uptake of 7.2% of the total ^{14}C activity in soybean leaves grown in soil aged 3 months. Uptake decreased to 2.9% in soil aged 24 months. The same soybean leaf sample (aged 3 months) was the only plant sample to exceed uptake of more than 3.9% of the total unextractable radioactivity.

DISCUSSION:

1. Low recovery of label precluded preparation of a material balance. It is not known whether conditions changed from aerobic to anaerobic when the jars were sealed. However, it is assumed that most of the initial degradation occurred under aerobic conditions.
2. The aqueous photolysis study was inadequate because it was conducted in nonsterile tapwater.
3. The experimental procedures and protocols for the soil-water photodegradation study were not acceptable because there was no mention of monitoring ^{14}C activity in the aqueous phase. Therefore, the amount of radioactivity actually adsorbed to the soil is not known.

4. The runoff study indicates minimal losses after aging and soil drenching, however, the study was not performed in a manner which delineates leaching per se.
5. The confined accumulation study cannot be used to determine uptake of fonofos residues by rotational crops because the experiment was conducted using aged soil with no extractable residues. For this reason, the study is unacceptable.
6. The Felton soil was reported as a sandy loam; however, it is actually a loamy sand according to USDA's textural classification system and was reported as such in this review.

Table 1. Degradates recovered from soil treated with labeled [^{14}C]fonofos^a at indicated intervals.

Degradate	Exposure (months)							
	3		12		15		24	
	Ethoxy ^b	Phenyl ^c	Ethoxy	Phenyl	Ethoxy	Phenyl	Ethoxy	Phenyl
Fonofos	41.5	46.5	24.8	21.1	26.9	17.5	18.8	14.9
Fonofos oxon	0.1	0.5	--	0.1	0.03	0.03	0.1	0.4
<u>O</u> -Ethylethane phosphonothioic acid	4.2	--	6.0	--	8.1	--	8.1	--
<u>O</u> -Ethylethane phosphonic acid	--	--	0.9	--	3.2	--	1.3	--
<u>O</u> -Ethyl <u>O</u> -methyl ethyl-phosphonate	0.1	--	--	--	0.3	--	--	--
Diphenyl disulfide	--	0.8	--	1.1	--	3.0	--	2.4
Methylphenyl sulfoxide	--	0.2	--	0.2	--	0.2	--	--
Methylphenyl sulfone	--	--	--	0.1	--	0.1	--	--
Unknowns	4.4	5.1	6.2	5.1	2.0	6.9	0.4	0.7
Unextractable	19.9	32.5	25.5	54.8	15.2	48.9	19.0	35.1
Total	70.2	85.6	63.4	82.5	55.5	76.5	47.7	53.5

^aExpressed as percent of total added label recovered.

^b1-Ethoxy-labeled [^{14}C]fonofos.

^cPhenyl-labeled [^{14}C]fonofos.

CASE GS 0105

FONOFOS

STUDY 3

PM 300 07/15/82

CHEM 041701

Fonofos

BRANCH EFB

DISC 30 TOPIC 050520

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID 00092024

CONTENT CAT 01

Hoffman, L.J., and J.H. Ross. 1971. Dyfonate soil metabolism: Project 038022. Unpublished study received Nov. 1, 1971 under OF0960; submitted by Stauffer Chemical Co., Richmond, Calif.; CDL:094505-D.

SUBST. CLASS = S.

DIRECT RVW TIME = 4

(MH) START-DATE

END DATE

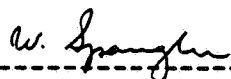
REVIEWED BY: W. Spangler

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DATE: Nov. 16, 1982

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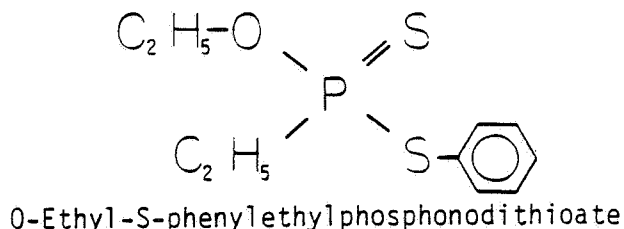
CONCLUSIONS:

Metabolism - Aerobic Soil

1. This study is scientifically valid.
2. Fonofos is degraded in a sandy loam soil with a half-life of ~3 months; 22-28% of the applied radioactivity remained as parent compound after 15 months. Major degradates detected were O-ethylethane phosphonothioic acid (6.9% of applied radioactivity) and diphenyl disulfide (2.9% of applied radioactivity). Most of the radioactivity added (60-72%) was unrecoverable after 15 months.
3. This study partially fulfills EPA Data Requirements for Registering Pesticides (1983) by providing half-life data and by identifying two fonofos degradates in sandy loam soil incubated under aerobic conditions

MATERIALS AND METHODS:

FONOFOS, DYFONATE, N-2788



Felton loamy sand soil (94% sand, 4% silt, 2% clay, 2% organic matter, pH 5.7, 5% moisture, and CEC 7.5 meq/100 g) was collected, sieved through a 6-mm mesh screen, and treated with 1-ethoxy-labeled or phenyl-labeled [^{14}C]fonofos (>99% radiochemical purity, Stauffer Chemical Co.) at 10 ppm. The lots were divided into 1-kg samples which were sealed in jars, stored in a greenhouse at 21-25 C, and sampled for analysis after 3, 12, and 15 months. Residues were extracted with 50% aqueous ethanol until radioactivity ceased to elute, then combined extracts were partitioned with dichloromethane. Aqueous and organosoluble fractions were radioassayed by using LSC, concentrated by vacuum evaporation, and metabolites analyzed by co-chromatography with reference standards. Radioactive spots were scraped from TLC plates and quantified by using LSC.

REPORTED RESULTS:

Fonofos was degraded in soil with a half-life of ~ 3 months. After 15 months, only 40.3% of the 1-ethoxy-labeled [^{14}C]fonofos and 27.7% of the phenyl-labeled [^{14}C]fonofos added was recoverable as aqueous and organosoluble residues. Of the applied activity, 22-28% remained as parent compound after 15 months. The major degradate detected from 1-ethoxy-labeled [^{14}C]fonofos was O-ethylethane phosphonothioic acid (6.9% of applied activity at 15 months) and the major degradate detected from phenyl-labeled [^{14}C]fonofos was diphenyl disulfide (2.9% of applied after 15 months).

DISCUSSION:

1. The low recoverable activity was not acceptable for determination of a materials balance.
2. The Felton soil was reported as a sandy loam; however, it is actually a loamy sand according to USDA's textural classification system and was reported as such in this review.

CASE GS 0105 FONOPOS STUDY 4 PM 300 07/15/82

CHEM 041701 Fonofos

BRANCH EFB DISC 20 TOPIC 1015 GUIDELINE 40 CFR 163.62-8f3

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID 00073059 CONTENT CAT 01

Miles, J.R.W., C.M. Tu, and C.R. Harris. 1979. Persistence of eight organophosphorus insecticides in sterile and non-sterile 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, Mich.; CDL:238974-A.

SUBST. CLASS = S.

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

REVIEWED BY: M. Edwards and B. Gregg
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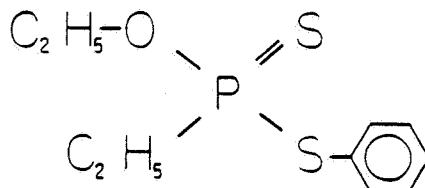
CONCLUSIONS:

Metabolism - Aerobic Soil

1. This study is scientifically valid.
2. Fonofos at 10 ppm showed greater persistence in sterile sandy loam and organic soils (half-life >24 weeks) than in nonsterile samples of the same soils (half-life 3-4 weeks).
3. This study partially fulfills EPA Data Requirements for Registering Pesticides (1983) by providing data on the half-life of fonofos in a sandy loam and organic soil.

MATERIALS AND METHODS:

FONOFOS, DYFONATE, N-2788



O-Ethyl-S-phenylethylphosphonodithioate

Sterile (autoclaved) and nonsterile samples of sieved (10-mesh) sandy loam (2.9% organic matter; pH 8.0) and organic soil (48.7% organic matter; pH 7.6) were treated with fonofos at 10 ppm (analytical grade, source unspecified). Sample bottles were covered with polyethylene film and incubated in the dark at 28 C and 60% water holding capacity. Fonofos levels were determined 0, 1, 2, 4, 8, 12, 16, 20, and 24 weeks after treatment. Fonofos was extracted from soil with acetone and benzene:hexane. Acetone was removed with distilled water, and the benzene:hexane extract dried and analyzed by using GLC as described by Miles et al. (1978. J. Econ. Entomol. 71:97). Average recovery of fonofos-spiked samples was 82% (sensitivity not reported).

REPORTED RESULTS:

In sterile soils, fonofos had a half-life >24 weeks, while half-lives in the nonsterile sandy loam and organic soil were 3 and 4 weeks, respectively.

DISCUSSION:

1. Experimental procedures and protocols were acceptable. Samples were run in triplicate with appropriate controls.
2. No effort was made to identify or quantitate any metabolites.

CASE GS 0105

FONOFOS

STUDY 5

PM 300 07/15/82

CHEM 041701

Fonofos

BRANCH EFB

DISC 30 TOPIC 050525

GUIDELINE 40 CFR 163.62-9b/c/d

FORMULATION 04 - GRANULAR

FICHE/MASTER ID 00090870

CONTENT CAT 01

Abdel-Gawaad, A.A.W., M.A. Hamad, and F.H. El-Gayer. 1971. Effect of the canal irrigation system used in the UAR on the persistence of soil insecticide. International Pest Control (Jul-Aug):8-10,28. Also In unpublished submission received Dec. 13, 1977 under 476-1995; submitted by Stauffer Chemical Co., Richmond, Calif.; CDL:232469-L.

SUBST. CLASS = S.

DIRECT RVW TIME = 4

(MH) START-DATE

END DATE

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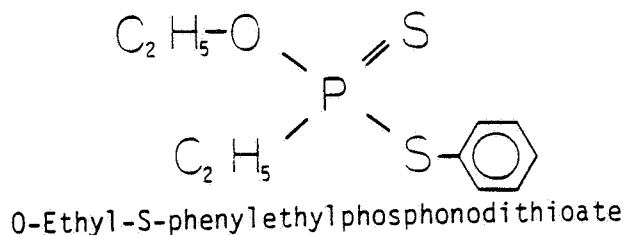
CONCLUSION:

Mobility - Leaching and Adsorption/Desorption

This study is invalid because leachates from untreated soil column controls were not included to verify that toxicity observed in treated leachates was due to fonofos residues. In addition, this study would not fulfill EPA Data Requirements for Registering Pesticides (1983) because a formulated product was used and not an analytical, technical, or purer grade chemical, and because a bio-assay was used to detect fonofos residues.

MATERIALS AND METHODS:

FONOFOS, DYFONATE, N-2788



Leaching of fonofos (5% G, Stauffer Chemical Co.) was studied in six soils of varying texture (Table 1). Each soil (4.5 kg) was placed in metal columns 80 cm in length x 32 cm I.D., in duplicate, and topped with a 0.25-kg layer containing 462 mg of fonofos. Columns were leached every 15 days with ~4.6 inches, leachate was collected for 24 hours following each application, and analysis for toxic residues were performed using a *Daphnia magna* Strauss bioassay described by Frear and Boyd (1967. J. Econ. Entomol. 80(5):1228-1236). Bioassays were performed on each of the five leachates per column by addition of 1 ml of leachate to 250 ml water containing 10 daphnids. Quadruplicate assays were scored for mortality after 24 hours exposure and compared to a standard mortality curve.

REPORTED RESULTS:

The percentage of fonofos leached through the columns was determined by comparing daphnid mortality determined in leachates to standard insecticide curves. The percent leached by ~23 inches of water (Table 1) ranged from 4.0% (clay soil) to 11.9% (calcareous sandy loam).

DISCUSSION:

1. Columns were not segmented following leaching to determine movement of fonofos residues within the soil columns. Failure to include appropriate untreated soil column controls for the daphnid bioassay invalidates the study because the toxicity observed in the leachate cannot be attributed to fonofos.
2. A formulated product was used and leaching was determined by using a bioassay procedures. These protocols are unacceptable.

Table 1. Soil characteristics and recovery of fonofos from leachates of soils.

Soil	Mechanical analysis (%)			pH	Organic matter (%)	Recovery in leachate (%) ^a
	Sand	Silt	Clay			
Sandy loam	75.0	10.0	15.0	7.4	1.5	8.9
Sandy clay loam	52.7	12.5	34.8	7.8	1.9	8.2
Calcareous sandy loam	54.3	9.8	35.9	7.2	0.9	11.9
Clay loam	35.6	24.7	39.7	7.5	0.3	5.7
Secka sandy clay loam	41.8	19.8	38.4	7.8	1.8	7.9
Clay	17.8	21.7	60.5	7.7	1.9	4.0

^aPercent by weight of total fonofos added as determined by using a daphnid bioassay.

CASE GS 0105

FONOFOS

STUDY 6

PM 300 07/15/8

CHEM 041701

Fonofos

BRANCH EFB

DISC 30 TOPIC 050520

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID 00052059

CONTENT CAT 01

Lichtenstein, E.P., K.R. Schulz, and T.W. Fuhremann. 1972. Movement and fate of Dyfonate in soils under leaching and nonleaching conditions. J. Agric. Food Chem. 20(4):831-838. Also In unpublished submission received April 2, 1973 under 3F1379; submitted by Stauffer Chemical Co., Richmond, Calif.; CDL:093686-C.

SUBST. CLASS = S.

DIRECT RVW TIME = 8

(MH) START-DATE

END DATE

REVIEWED BY: M. Peterson and R. Schaefer

TITLE: Staff Scientists

ORG: Dynamac Corp., Enviro Control Division, Rockville, MD

LOC/TEL: 468-2500

SIGNATURE:

DATE: Nov. 10, 1982

APPROVED BY:

TITLE:

ORG:

LOC/TEL:

SIGNATURE:

DATE:

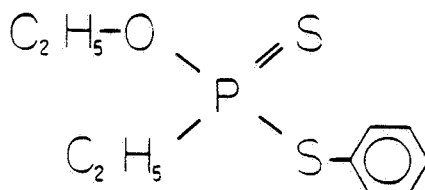
CONCLUSIONS:

Mobility - Leaching and Adsorption/Desorption

1. This study is scientifically valid.
2. Fonofos is relatively immobile in a silt loam and sandy loam soil and mobile in quartz sand. After leaching a 7-inch column of silt loam soil with 11.5 inches of water over 105 days, ~20% of the [¹⁴C]fonofos dose applied remained in the treated soil layer and ~2% was present in lower soil layers and in the leachate. When silt loam and sandy loam soils were leached with 6.9 inches of water over 17 days, ~37% of the fonofos applied remained in the treated soil layer, and ~9% was present in lower soil layers. When a quartz sand was leached under the same conditions, none of the applied radioactivity was in the sand and ~50% was in the leachate. Dyfoxon, a fonofos degradate, and two unidentified compounds were found in the leachate of the silt loam soil leached with 11.5 inches of water.
3. This study does not satisfy EPA Data Requirements for Registering Pesticides (1983) because the leaching columns were too short (7 inches) and an insufficient amount of water was leached through the columns (11.5 inches over 105 days). In addition, soil columns were too short and no K_d values were calculated.

MATERIALS AND METHODS:

FONOFOS, DYFONATE, N-2788



O-Ethyl-S-phenylethylphosphonodithioate

Ethoxy-labeled [^{14}C]fonofos (Dyfonate, specific activity 5.75 mCi/mmol, Stauffer Chemical Co.) was diluted with nonlabeled fonofos, (formulation and purity unspecified, Stauffer Chemical Co.), applied at 20 ppm to a silt loam soil (Table 1), and aged for 1 day in a sealed container in an incubator at 27 C. Soil columns were prepared in four 1-quart cartons (7 inches long, 3.5-inch diameter) by perforating the bottoms and layering glass wool and 200-g portions of hexane-washed quartz sand across them. A 200-g portion of treated soil, containing 13.5 $\mu\text{g/g}$ (0.011 $\mu\text{Ci/g}$) of [^{14}C]fonofos, was then layered in each carton above two 200-g portions of untreated silt loam. Quartz sand was added to the top of the column and covered with filter paper to improve water distribution over the soil surface. Perforated stainless steel plates were used to separate each 200-g layer. Water was added to each column at 1 drop/5 seconds until saturation. Leaching was continued until 330 ml of water (equivalent to ≈ 2.3 inches of water) was collected from each column. A 250-ml aliquot of this water was extracted and analyzed while an 80-ml aliquot was used for bioassay tests with mosquito larvae. The soil columns were then incubated 14 days at 27 C, after which leaching was repeated (day 15). Following another 14-day incubation, leaching was repeated (day 29). Two of the four cartons were then frozen, and the soil layers were removed, extracted, and analyzed along with the leachate collected. Leaching was repeated in the remaining two cartons 44 and 105 days after the initial fonofos treatment. Leachate and soil layers from the columns were then extracted and analyzed. The experiment was repeated using two soil columns, incubated for 29 days, to which ring-labeled [^{14}C]fonofos (Dyfonate, specific activity 4.7 mCi/mmol, Stauffer Chemical Co.) was applied at 20 ppm. Fonofos concentrations were 15 $\mu\text{g/g}$ (0.008 $\mu\text{Ci/g}$) in soil after a 1-day incubation.

In a second experiment, a silt loam, fine sandy loam, and quartz sand (Table 1) were treated with fonofos (Dyfonate, formulation and purity unspecified, Stauffer Chemical Co.) in acetone at 20 ppm. Aliquots of each soil were removed for initial analysis and the soils were then layered in duplicate columns as described above. Water was leached through the columns immediately, and following 7 and 17 days of incubation at 22 C. Soils, sand, and leachate were extracted and analyzed, and a portion of each was tested for insect toxicity using Drosophila or Aedes bioassays.

Soils were extracted twice with a 1:1 mixture of methyl alcohol and acetone, and once more with a 1:1:1 mixture of benzene methanol, and acetone. The remaining extract was shaken in benzene, yielding a benzene and water phase. The water phase was acidified with 1 N HCl and further extracted with diethyl ether to yield an ether fraction and a water fraction. Soils from the second experiment were extracted with a 1:1 mixture of hexane and acetone. Leachate from the first experiment was extracted with benzene while that from the second was extracted with hexane. The fonofos content of the soil and water extracts was analyzed by using LSC, GLC, and/or TLC. Insect toxicity was assayed using vinegar flies (*Drosophila melanogaster* Meig.) or mosquito larvae (*Aedes aegypti* L.).

REPORTED RESULTS:

Using GLC, 60% of the ethoxy-labeled fonofos detected in a treated silt loam 1 day after application was recovered as fonofos from the soil columns and leachate after 29 days incubation. [¹⁴C]Fonofos recovery was 28% after 105 days incubation, indicating that 72% of the radioactivity originally applied was lost during the 105-day period. Using LSC, 73 and 47% of the fonofos applied persisted in soil and water after 29 and 105 days, respectively. Of the radioactivity recovered from the soil layers, ~75% remained in the treated soil layer, ~25% was found in the first untreated layer, and <1% was detected in the bottom layer. Respectively, these amounts represented 45.0, 14.0, and 0.4% of the fonofos originally present after 29-day incubation, and 19.0, 1.5, and 0.3% after 105-day incubation. Fonofos did not move rapidly through soil columns, 1.5% of the original amount was detected in the leachate after three leachings, and 2.1% after five leachings. With one anomalous exception, the water was not toxic to mosquito larvae. Discrepancies between data obtained by using GLC and LSC suggested that some fonofos metabolism had occurred; TLC and autoradiography indicated that dyfoxon was also present in the leachate from the ring-labeled fonofos treatment, 90.2% of the originally present radiocarbon was recovered from soil and water after the 29-day incubation. TLC analysis of these samples indicated that water leached through the ring-labeled fonofos treatments contained fonos (R_f 0.70), dyfoxon (R_f 0.42), and two unknown substances (R_f 0.22 and 0.53).

The second experiment showed that leachate from the silt loam contained no fonofos and was not toxic to mosquito larvae. Of the 46% of the original dose present in the soil column after 17 days, ~80% was located in the treated layer, ~20% was in the upper untreated layer, and <1% was detected in the lower untreated layer. Total amounts of fonofos recovered from the sandy loam were similar to amounts found in the silt loam; however, both untreated layers contained amounts approximately equivalent to those detected in the treated layer. Leachate initially contained only trace amounts of fonofos, and was not toxic to insects; however, fonofos levels and insect mortality increased steadily with subsequent leachings. Fonofos

recovery from the quartz sand was 52.35% of the original amount applied; 52.2% of the original amount was detected in the leachate. The mosquito bioassays and GLC analyses indicated that >67% of the amount recovered had leached through the column with the first leaching.

DISCUSSION:

1. Soil pH and moisture content were not reported.
2. Recoveries for most experiments reported were low (50% or less). No discussion or explanation of loss of radioactivity was given.

Table 1. Soil characteristics.

Soil	Mechanical Analysis (%)			Organic matter (%)
	Sand	Silt	Clay	
Plano silt loam	5	71	24	4.7
Fox fine sandy loam	84	12	4	1.0
Quartz sand	100	0	0	0.0

CASE GS 0105

FONOFOS

STUDY 7

PM 300 07/15/82

CHEM 041701

Fonofos

BRANCH EFB

DISC 30 TOPIC 101050

FORMULATION 90 - FORMULATION NOT IDENTIFIED

FICHE/MASTER ID 00079801

CONTENT CAT 03

Kadoum, A.M., and D.E. Mock. 1978. Herbicide and insecticide residues in tailwater pits: water and pit bottom soil from irrigated corn and sorghum fields. J. Agric. Food Chem. 26 (1):45-50. Also In unpublished submission received on unknown date under 352-338; submitted by E.I. du Pont de Nemours and Co., Wilmington, Del.; CDL:236741-R.

SUBST. CLASS = S.

DIRECT RVW TIME = 5

(MH) START-DATE

END DATE

REVIEWED BY: J. MacPherson, Jr. and R. Schaefer

TITLE: Staff Scientists

ORG: Dynamac Corp., Enviro Control Division, Rockville, MD

LOC/TEL: 468-2500

SIGNATURE:

J.R. MacPherson Jr. R. Schaefer

DATE: Nov. 5, 1982

APPROVED BY:

TITLE:

ORG:

LOC/TEL:

SIGNATURE:

DATE:

CONCLUSIONS:

Field Dissipation - Aquatic and Aquatic Impact

1. This monitoring study is scientifically valid.
2. Fonofos was detected in tailwater pit sediments and water during 1973 and 1974 in Haskell county, Kansas. The highest concentrations found were 770 ppb for sediment and 5.9 ppb for water during 1974. Mean peak concentrations were highest in June and July.
3. This study does not fulfill EPA Data Requirements for Registering Pesticides (1983) because currently there are no requirements for the submission of monitoring data.

DISCUSSION:

It was reported that interviews were conducted and questionnaires were sent out to determine actual pesticide applications on the various fields. None of these data were presented

CASE GS0105

FONOFOS

STUDY 8

PM 300 07/15/82

CHEM 041701

Fonofos

BRANCH EFB

DISC 30 TOPIC 05

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID 00090826

CONTENT CAT 01

Lichtenstein, E.P., and K.R. Schulz. 1970. Volatilization of insecticides from various substrates. J. Agric. Food Chem. 18(5):814-818. Also In unpublished sub- mission received Nov. 1, 1971 under OF0960; submitted by Stauffer Chemical Co., Richmond, Calif.; CDL:094505-E.

SUBST. CLASS = S.

DIRECT RVW TIME = 6

(MH) START-DATE

END DATE

REVIEWED BY: M. Peterson and R. Schaefer

TITLE: Staff Scientists

ORG: Dynamac Corp., Enviro Control Division, Rockville, MD

LOC/TEL: 468-2500

SIGNATURE:

DATE: Nov. 9, 1982

APPROVED BY:

TITLE:

ORG:

LOC/TEL:

SIGNATURE:

DATE:

CONCLUSIONS:

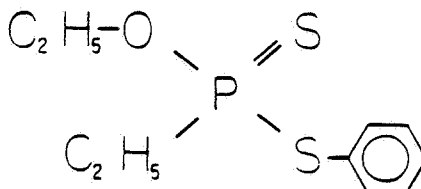
Mobility - Laboratory Volatility

1. This study is scientifically valid.
2. Fonofos volatility, within 24 hours after application, as a percentage of the amount applied, was greatest from soil water (16.3%) and tap water (15.2%), and less from a silt loam soil (1.0%). The quantities of fonofos volatilized from soil water increased in proportion with application rate over the 2.5-20 ppm range, but showed a relative decrease over the 40-160 ppm concentration range. The half-life for a 12.5 ppm fonofos application to soil water was 4.8 days; 80% of the original amount was volatilized at the end of 10 days. ←
3. This study does not satisfy EPA Data Requirements for Registering Pesti- cides (1983) because the test substance employed was not a typical end-use product.

-2-

MATERIALS AND METHODS:

FONOFOS, DYFONATE, N-2788



O-Ethyl-S-phenylethylphosphonodithioate

[¹⁴C]Fonofos (Dyfonate analytical grade, Stauffer Chemical Co., specific activity unspecified) in ethanol was added to glass flasks containing one of the following experimental substrates: tap water, soil water (a fine soil suspension in tap water), and silt loam soil. Diethylether was added to facilitate [¹⁴C]fonofos distribution on soil. Following solvent evaporation, insecticide vapor traps (0.5 g of borosilicate glass wool treated with 5% corn oil in hexane) were sealed to the top of each flask and covered with aluminum foil. Flasks and traps were placed in a water bath shaker and incubated at 30 C for 24 hours. Traps were then removed from their respective flasks, placed on empty flasks, and washed with two 10-ml portions of hexane and forced air. The hexane extracts were analyzed for fonofos by using LSC and GLC. Recovery experiments indicated that 93.2% of the radioactivity in the applied dose was detected by using this method.

For the second experiment [¹⁴C]fonofos in hexane was added to soil water at 2.5, 5, 10, 20, 40, 80, or 160 ppm. Vapor traps were placed over the flasks, incubated at 30 C for 24 hours, and analyzed by using LSC.

In the third experiment, [¹⁴C]fonofos at 12.5 ppm was added to 2 ml of soil water in each of 24 flasks. Vapor traps were placed on the flasks, and analyzed by using LSC and GLC after 0, 2, 3, 4, 5, 6, 8, and 10 days of incubation at 30 C. Analysis of each sample was repeated by using TLC and autoradiography. Two or three replications were made of each treatment in all of the experiments.

REPORTED RESULTS:

Volatilization was 14-16 times greater from tap water and soil water than from soil (Table 1). Fonofos was volatilized in linearly increasing amounts from soil water treated at 2.5, 5.0, 10, and 20 ppm, although the percentage volatilized remained within the range of 16 to 21% of that applied. As fonofos concentrations in soil water increased further, the actual amounts volatilized showed a relative decline. The percentages of applied fonofos volatilized at 40, 80, and 160 ppm in soil water were 10.3, 4.6, and 2.0%, respectively. The amounts of fonofos volatilized from treated soil water after 1-10 days of incubation increased with time, while the rate of volatilization declined

over time. The volatilization rate was greatest during the first 2 days of incubation (slope = 2.72) and least during the 6- to 10-day period (slope = 0.22). Fifty percent of the radioactivity applied was volatilized after 4.8 days and, after 10 days, only 20% of the applied dosage remained in the soil water. Results obtained by using LSC were generally higher than those obtained by using GLC; TLC and autoradiography procedures indicated the presence of two additional ^{14}C -containing compounds, polar metabolites of fonofos.

DISCUSSION:

1. The specific activity of the radiolabeled test substance was not reported.
2. Soil adsorption coefficients (K_d) were not reported for the test soil employed.

Table 1. Volatilization of fonofos from various substrates at 30 C.

Substrate	<u>Volatility as % of amount applied/24 hours</u>	
	LSC	GLC
Tap water	15.2	15.0
Soil water	16.3	14.0
Silt loam soil	1.0	0.80

CASE GS 0105

FONOFOS

STUDY 9

PM300 07/15/82

CHEM 041701

Fonofos

BRANCH EFB

DISC 30 TOPIC 050530

GUIDELINE 40 CFR 163.62-10b

FORMULATION 04 - GRANULAR

FICHE/MASTER ID 00090869

CONTENT CAT 01

Ahmed, J., and F.O. Morrison. 1972. Longevity of residues of four organophosphate insecticides in soil. *Phytoprotection* 53(2-3):71-74. Also In unpublished submission received Dec. 13, 1977 under 476-1995; submitted by Stauffer Chemical Co., Richmond, Calif.; CDL:232469-K.

SUBST. CLASS = S.

DIRECT RVW TIME = 3

(MH) START-DATE

END DATE

REVIEWED BY: M. Peterson and R. Schaefer

TITLE: Staff Scientists

ORG: Dynamac Corp., Enviro Control Division, Rockville, MD

LOC/TEL: 468-2500

SIGNATURE: *M. Peterson*

R. Schaefer

DATE: Nov. 9, 1982

APPROVED BY:

TITLE:

ORG:

LOC/TEL:

SIGNATURE:

DATE:

CONCLUSIONS:

Field Dissipation - Terrestrial

1. This study is scientifically valid.
2. Toxic fonofos residues, as measured by a root maggot bioassay, dissipated more quickly from sandy loam field plots than from plots maintained in the greenhouse. At a dose of 6 lb/A, toxic residues were detected for up to 17 weeks in the field and 28 weeks in the greenhouse. ←
3. This study does not satisfy EPA Data Requirements for Registering Pesticides (1983) because a bioassay was used.

CASE GS 0105 FONOFOF STUDY 10 PM 07/15/82

CHEM 041701 Fonofos

BRANCH EFB DISC 30 TOPIC 050530 GUIDELINE 40 CFR 163.62-10b

FORMULATION 12 - EMULSIFIABLE CONCENTRATE (EC OR E)

FICHE/MASTER ID 00090827 CONTENT CAT 01

Kiigemagi, U., and L.C. Terriere. 1971. The persistence of Zinophos and Dyfonate in soil. Bull. Environ. Contam. Toxicol. 6(4):355-361. Also In unpublished submission received Nov. 1, 1971 under OF0960; submitted by Stauffer Chemical Co., Richmond, Calif.; CDL:094505-F.

SUBST. CLASS = S.

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

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

SIGNATURE: *B. Gregg* *R. Schaefer* DATE: Nov. 8, 1982

APPROVED BY:
TITLE:
ORG:
LOC/TEL:

SIGNATURE: DATE:

CONCLUSIONS:

Field Dissipation - Terrestrial

1. This study is scientifically valid.
2. Fonofos dissipated with a half-life of ~40 days when the 4 lb/gal EC formulation was applied at 4.78 lb ai/A to Newberry sandy loam soil.
3. This study partially fulfills EPA Data Requirements for Registering Pesticides (1983) by providing fonofos dissipation data in a sandy loam.

Table 1. Dissipation of fonofos applied to a sandy loam soil in Oregon^a.

Days after treatment	Fonofos concentration (ppm)	% of original concentration	Accumulated rainfall (inches) ^b
0	2.05	100	--
1	1.92	94	0.05
3	1.81	88	0.09
7	1.52	74	0.07
14	1.18	58	0.00
28	1.11	54	0.29
56	0.95	46	0.00
84	0.79	39	0.00
120	0.55	27	5.10

^aMean of six replicate plots treated with 4 lb/gal EC at 4.78 lb ai/A.

^bDuring that sampling interval.

CASE GS0105

FONOFOS

STUDY 11

PM 300 07/15/82

CHEM 041701

Fonofos

BRANCH EFB

DISC 30 TOPIC 050530

GUIDELINE 40 CFR 163.62-10b

FORMULATION 12 - EMULSIFIABLE CONCENTRATE (EC OR E)

FICHE/MASTER ID 00041235

CONTENT CAT 01

Schulz, K.R., and E.P. Lichtenstein. 1971. Field studies on the persistence and movement of Dyfonate in soil. J. Econ. Entomol. 64(1):283-287. Also In unpublished submission received July 24, 1974 under 3F1379; submitted by Stauffer Chemical Co., Richmond, Calif.; CDL:092139-F.

SUBST. CLASS = S.

DIRECT RVW TIME = 5

(MH) START-DATE

END DATE

REVIEWED BY: B. Gregg and R. Schaefer

TITLE: Staff Scientists

ORG: Dynamac Corp., Enviro Control Division, Rockville, MD

LOC/TEL: 468-2500

SIGNATURE:

DATE: Nov. 10, 1982

APPROVED BY:

TITLE:

ORG:

LOC/TEL:

SIGNATURE:

DATE:

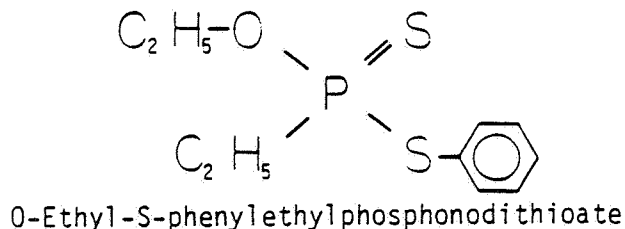
CONCLUSIONS:

Field Dissipation - Terrestrial

1. This study is scientifically valid.
2. Fonofos dissipates fairly rapidly in a silt loam soil; a half-life of ~28 days was found when fonofos 4 lb/gal EC was applied at 10 lb/A. No degradates of fonofos were detected. ←
3. This study partially fulfills EPA Data Requirements for Registering Pesticides (1983) by providing fonofos dissipation data in a silt loam soil.

MATERIALS AND METHODS:

FONOFOS, DYFONATE, N-2788



Fonofos (Dyfonate 4 lb/gal EC, Stauffer Chemical Co.) was applied broadcast at 10 lb/A to Carrington silt loam soil (characteristics not provided) near Madison, Wisconsin. Samples were collected from thirty 6-inch cores at 0, 1, 2, 3, 4, 10, 16, and 22 months after treatment. The samples were extracted with a hexane:acetone 1:1 mixture and analyzed by using GLC with an electron capture detector (minimum detection level and percent recovery data not reported). TLC analyses were also performed on soils collected at 1, 2, 3, 4, and 16 months post-treatment. The hexane:acetone extracts were processed by using a clean-up procedure (Storherr and Watts, 1965. J. Assoc. Offic. Agric. Chem. 48(6):1154-1158), then concentrated and spotted on TLC plates (developed with ethyl acetate and visualized with palladium chloride). Fonofos and three probable degradates (thiophenol, dyfoxon, and ethylethoxythiophosphonic acid; standards for all four chemicals obtained from Stauffer Chemical Co.) were spotted and compared against soil extract TLC plates; the minimum detection limit was 3 µg for each chemical and recoveries were calculated (percentages not reported) for soil extracts of all four chemicals spiked at 1 ppm (except ethylethoxythiophosphonic acid recovered only to a small extent).

REPORTED RESULTS:

The half-life of fonofos was about 28 days, with 3.39 ppm reported for the 1 month sampling compared with 7.07 ppm for the initially recovered level of 7.07 ppm sampled immediately after application. After 4 months, 24% of the 10 lb/A applied was found; from this October sampling to early the next spring (April; 10 months post-treatment), there was no further decline in fonofos concentration. The fonofos level had dissipated at 16 months post-treatment to 7.7% of the applied rate (0.50 ppm) and at 22 months to ~6%. On TLC plates, only fonofos was detected, and not any of the three probable degradates.

DISCUSSION:

It was reported that additional experiments had been performed with the 4 lb/gal EC formulation broadcast and rototilled onto soil, to test absorption and accumulation by growing plants (carrots and potatoes); but insufficient data were presented concerning planting time and treatment intervals, so these studies could not be evaluated.

CASE GS 0105 FONOPOS STUDY 12 PM 300 07/15/82

CHEM 041701 Fonofos

BRANCH EFB DISC 30 TOPIC 050530 GUIDELINE 40 CFR 163.62-10b

FORMULATION 04 - GRANULAR

FICHE/MASTER ID 00090871 CONTENT CAT 01
Talekar, N.S., L.T. Sun, E.M. Lee, and J.S. Chen. 1977. Persistence of some insecticides in subtropical soil. J. Agric. Food Chem. 25(2):348-352. Also In unpublished submission received Dec. 13, 1977 under 76-1995; submitted by Stauffer Chemical Co., Richmond, Calif.; CDL:232469-M.

SUBST. CLASS = S. OTHER SUBJECT DESCRIPTORS SEC: RCBR-25-10366010 RCBR-25-10479010

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

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

SIGNATURE: M. Pete DATE: Nov. 9, 1982

APPROVED BY:
TITLE:
ORG:
LOC/TEL:

SIGNATURE: DATE:

CONCLUSIONS:

Field Dissipation - Terrestrial

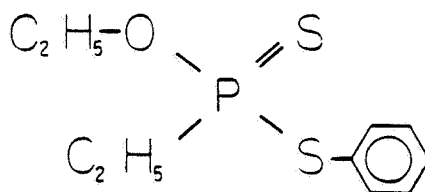
- 1. This study is scientifically valid.
2. Fonofos dissipates rapidly from a subtropical silt loam soil. After an autumn application of the 10% G formulation 10 kg ai/ha, 64 and 92% of the fonofos applied had dissipated within 6 and 18 weeks, respectively. Following a second application in spring, 99.3% of the fonofos applied had dissipated by the time of autumn harvest 5 months later. Fonofos degradates were not detected in any of the soil samples.
3. This study partially satisfies EPA Data Requirements for Registering Pesticides (1983) by showing that fonofos dissipates rapidly from a silt loam soil, with no appreciable accumulation of degradates.



-2-

MATERIALS AND METHODS:

FONOFOS, DYFONATE, N-2788



O-Ethyl-S-phenylethylphosphonodithioate

Fonofos (10% G, source unspecified) was applied to field plots (sub-tropical conditions) at 10 kg ai/ha in fall and spring. The test soil was a silt loam (35.7% sand, 40.0% silt, 16.3% clay, pH 8.5-8.7, CEC 7.4 meq/100 g, 0.54% total carbon). Each plot was subdivided into three sections, with white potato or sweet potato planted in the center strip immediately after the fall application and the two outlying strips left fallow. Only sweet potato was planted following the spring application. The plots were regularly sprinkler-irrigated and were fertilized once each season. Untreated control plots were prepared and two replications of each treatment were made. Soil was sampled to a depth of 15 cm 1 day before fonofos application to determine the presence of any pesticide residues already in the soil. Soils were sampled immediately after the autumn application, at 6 weeks, at the end of the first growing season, and, following the spring application, at the end of the second growing season. Soil cores were removed at the intersections of a 1-meter grid, composited, and stored at -20 C before analysis. Thawed 250-g soil samples were extracted with a 1:1:1 mixture of methanol:acetone:benzene in a 1-liter glass jar. Fonofos was partitioned with ethyl acetate and analyzed by using GLC with an alkali flame ionization detector sensitive to phosphorus. The fonofos determinations were confirmed at the end of each growing season by using TLC.

REPORTED RESULTS:

Fonofos degraded rapidly in the silt loam soil. Six weeks after the initial treatment, 36% of the original amount applied remained in the soil. By the beginning of the next growing season (18 weeks post-treatment), 92% of the fonofos applied had dissipated from the soil. At the end of the second growing season, ~0.7% of the fonofos applied in spring was recovered. Both GLC and TLC analyses indicated that the degradate fonofos-oxon was not present in any of the soil samples.

DISCUSSION:

1. Soil samples were not taken at incremental depths from field plots.

2. Field plot grade was not specified.
3. Results from the control and pre-application soil samples were not reported.
4. Mechanical analysis of the test soil did not add up to 100%; however, it is assumed that a typographical error was made and that the soil was a silt loam.

CASE GS 0105 FONOPOS STUDY 13 PM 300 07/15/82

CHEM 041701 Fonofos

BRANCH EFB DISC 20 TOPIC 0510 GUIDELINE 40 CFR 163.63-8f2

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID 00090866 CONTENT CAT 01
Lichtenstein, E.P., H. Parlar, F. Korte, and A. Suss. 1977. Identification of fonofos metabolites isolated from insecticide-treated culture media of the soil fungus Rhizopus japonicus. J. Agric. Food Chem. 25(4):845-848. Also In unpublished submission received Dec. 13, 1977 under 476-1995; submitted by Stauffer Chemical Co., Richmond, Calif.; CDL: 232469-H

SUBST. CLASS = S.

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

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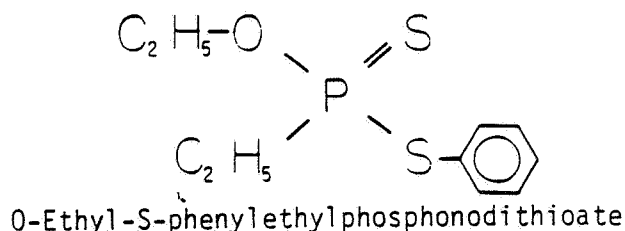
CONCLUSIONS:

Metabolism - Aerobic Soil

- 1. This study is scientifically valid and provides useful information by identifying several fonofos metabolites.
2. The soil fungus Rhizopus japonicus rapidly degraded [14C]fonofos in broth cultures at 27 C. In addition to several unidentified metabolites, the following metabolites were identified: dyfoxon (O-ethyl-S-phenylethyl phosphonothiolate), thiophenol, ethylethoxy phosphonic acid, and methylphenyl sulfoxide. Diphenyl sulfide, and O-ethyl-S-phenylmethyl phosphonodithioate were present as impurities in the starting material and in the cultures. O-ethyl-S-phenylmethyl phosphonothiolate was identified in cultures, and may have been derived from the latter impurity.
3. This study does not fulfill EPA Data Requirements for Registering Pesticides (1983) because there are currently no requirements for studies using pure cultures of microorganisms.

MATERIALS AND METHODS:

FONOFOS, DYFONATE, N-2788



All chemicals used in this study were analytical grades and supplied by Stauffer Chemical Company. The ethoxy-labeled [^{14}C]fonofos solution contained 3% impurities, one of which had a molecular weight of 280. The ring-labeled [^{14}C]fonofos solution contained 1.2% of the above mentioned impurity and O-ethyl-S-phenylmethylphosphonodithioate (Compound 3, Table 1), and 0.5% diphenyl sulfide (Compound 7, Table 1). The fungus *Rhizopus japonicus* was grown in a mineral salts glucose medium. An initial experiment was conducted to determine the rate of degradation of ethoxy-labeled [^{14}C]fonofos. To flasks containing 25 ml of media, a mixture of nonlabeled and radiolabeled fonofos was added at 0.4 ppm. The media were inoculated with spore suspensions prepared from agar slants, and incubated on a reciprocal shaker at 27 C for 1, 2, and 4 days. At each time point, the ^{14}C content in the water and hexane phases was determined as described below. Uninoculated control flasks were similarly incubated and analyzed.

To isolate metabolites, cultures were treated with a mixture of non-labeled and ethoxy- or ring-labeled [^{14}C]fonofos at 4 ppm, and incubated for 4 days on a shaker at 27 C. Uninoculated flasks were similarly incubated. The mycelium in each culture was then filtered, and the media was twice extracted with hexane:water (1:1). The ^{14}C content in each phase was determined by using LSC. In addition, two flasks were removed for analyses after 3 days, and the ^{14}C in the mycelia was determined at this time by combustion to $^{14}\text{CO}_2$. The hexane phase was evaporated for chemical analysis. The water phase was freeze-dried, and the yellowish powder so obtained was refluxed with acetone, filtered, and concentrated. No appreciable amounts of ^{14}C were lost during these procedures. The concentrated phases were analyzed by using GLC, and by TLC using two developing systems. TLC plates were radioscanned, and zones on the plates were scraped for structural analyses using a GC-MS instrument interfaced with a computer.

REPORTED RESULTS:

In initial experiments with ethoxy-labeled [^{14}C]fonofos, 83% of the applied ^{14}C was water soluble and no ^{14}C was determined in the hexane phase after 4 days of incubation with *R. japonicus*. In uninoculated controls, 6% was water soluble, and 75% remained in the hexane phase.

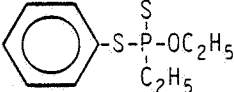
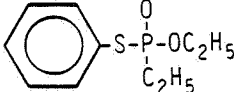
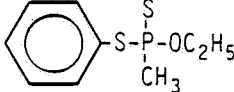
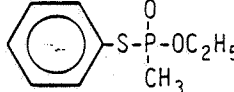
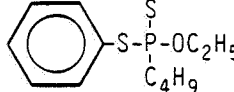
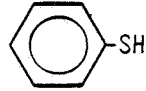
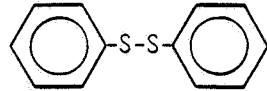
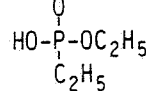
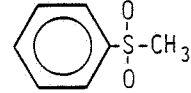
In a subsequent experiment, 3-day old cultures yielded 9% of the applied ^{14}C in the hexane phase, 55% in the water phase, and 22% in the mycelia. After 4 days, 69% of the applied ^{14}C was associated with the water phase, and only 3% with the hexane phase.

Two metabolites were isolated and identified from the water extracts of ethoxy-labeled [^{14}C]fonofos-treated cultures; these were Compounds 2 (dyfoxon) and 8 (Table 1). The water extracts of ring-labeled [^{14}C] fonofos-treated culture media contained eight compounds separable by TLC. The TLC plate was divided into zones, and the percent of total ^{14}C was determined for each zone. Zone I, which contained 29% of the total ^{14}C , contained a compound of unknown structure with a molecular weight of 190. Compound 9 (Table 1) was present in Zone II, which contained 45% of the total ^{14}C . Compounds 2, 3, 4, and 6 (Table 1) were present in Zone IX, which contained 9% of the total ^{14}C . Zone VII, which contained no measurable ^{14}C , had Compounds 1 (fonofos) and 5 (Table 1). Interference from biological material made it impossible to identify compounds in three other zones that contained 10% of the total ^{14}C . It was stated that only Compounds 2, 5, 8, and 9 represented actual metabolites of fonofos. Compounds 3 and 7 were present as impurities in the standard solutions, and Compound 4 was probably not formed from fonofos, but rather from Compound 3.

DISCUSSION:

1. Quantitative data were not obtained to determine if levels of Compounds 3 and 7 in 4-day old cultures were greater than the levels seen in the standard solution. These data would assist in fortifying or invalidating the hypothesis that their presence (and that of Compound 4) in cultures was due to the fact that they were present as impurities at the start of the study.
2. No explanation was provided to explain the presence of Compound 5 in the cultures.
3. The results concerning the metabolites were stated to have been obtained with water extracts. Although procedures were presented for the analysis of hexane extracts by using GLC, no specific data were presented for metabolites in the hexane extracts.

Table 1. Compounds identified in [^{14}C]-fonofos-treated cultures of Rhizopus japonicus.

Compound No.	Structure
1	
2	
3	
4	
5	
6	
7	
8	
9	

CASE GS 0105 FONOPOS STUDY 14

PM300 07/15/83

CHEM 041701 Fonofos

BRANCH EFB DISC --

FORMULATION 01 - TECHNICAL CHEMICAL

FICHE/MASTER ID - No MRID - CONTENT CAT --

Bionomics, Inc. 1972. Exposure of fish to ¹⁴C-labeled Dyfonate, accumulation, distribution and elimination of residues. Unpublished study received Apr. 3, 1973 under OF0960, submitted by Stauffer Chemical Co., Richmond, Calif.

SUBST. CLASS = --

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

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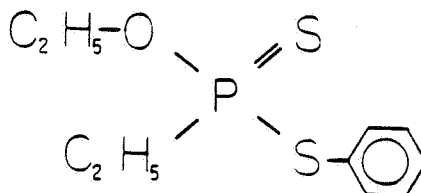
CONCLUSIONS:

Accumulation - Laboratory Fish

1. This study is scientifically valid.
2. Radioactive residues in the edible portion of bluegill sunfish exposed to [¹⁴C]-fonofos at 0.0017 mg/l reached a maximum of 0.25 mg/kg after 21 days. This value represents a bioconcentration factor of 150 X. By the end of the accumulation period (35 days), seven times more ¹⁴C was accumulated in visceral tissue (1.8 mg/kg) than in muscle (0.25 mg/kg). Accumulated ¹⁴C residues were depurated rapidly from edible tissue; after 3 days in untreated water, ~80% of the accumulated [¹⁴C]fonofos residues were eliminated. ←
3. This study partially fulfills EPA Data Requirements for Registering Pesticides (1983) by providing information on the accumulation and depuration of [¹⁴C]fonofos in the edible portion of bluegill sunfish tissue. However, total residues were quantified in viscera only on day 35 of the accumulation period, and were not quantified in whole fish at any time. Residues were not identified.

MATERIALS AND METHODS:

FONOFOS, DYFONATE, N-2788



O-Ethyl-S-phenylethylphosphonodithioate

Bluegill sunfish (*Lepomis macrochirus*) were acclimated for 7 days in 30-liter aquaria designed for flow-through aquatic conditions (flow rate 6 l/hr) at 18 ± 0.5 C. Ring-labeled [^{14}C]fonofos (Dyfonate technical, 94.4% purity, Stauffer Chemical Co.) was then introduced intermittently into the system to maintain an exposure concentration of 0.005 mg/l throughout the accumulation period of 35 days. Fish remaining at this time were transferred to untreated flowing water for a 14-day depuration period. Fish and water samples were taken from test and control aquaria at 1, 3, 7, 10, 14, 21, 28, and 35 days during the accumulation phase, and fish samples at days 1, 3, 7, 10, and 14 of depuration. Water was also sampled at day 0 of the accumulation phase.

Duplicate samples of fish tissue (muscle) were dried and combusted. The resulting $^{14}\text{CO}_2$ was trapped in ethanolamine, flushed with methanol (47%, v:v), and quantified by using LSC. Recovery values were 98-101%. To determine the relative distribution of polar and non-polar residues, muscle and viscera samples were extracted three times with hexane, and the extracts were filtered, combined, and evaporated. The concentrated extracts were then reextracted three times with methanol, and quantified by using LSC. Water samples were extracted four times with methylene chloride, and the extracts were combined, concentrated, and quantified by using LSC. Minimum detection limits were 0.005 mg/kg for fish, and 0.0001 mg/l for water.

REPORTED RESULTS:

The concentration of [^{14}C]fonofos in the edible tissue of bluegill sunfish reached maximum levels (0.24-0.25 mg/kg) between 21 and 35 days of exposure (Table 1). Based on the mean concentration of [^{14}C]fonofos in the water (0.0017 mg/l), this represented a bioconcentration factor of 150 X. Accumulated [^{14}C]fonofos in viscera was 1.8 mg/kg after 35 days of exposure. Approximately 80% of the accumulated [^{14}C]fonofos was eliminated from edible tissue during the first 3 days of depuration.

DISCUSSION:

1. Radioactive residues were not characterized.

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2. Total residues were not quantified in whole fish, and were quantified in visceral tissue only on day 35 of the accumulation period.

Table 1. Mean^a [¹⁴C]fonofos residues in bluegill sunfish and water during accumulation and depuration periods.

Phase/Day	Water (mg/l)	Muscle (mg/kg)	Viscera (mg/kg)
Accumulation 0	0.0017	--	--
1	0.0017	0.05	--
3	0.0017	0.097	--
7	0.0012	0.058	--
10	0.0012	0.088	--
14	0.0012	0.093	--
21	0.0019	0.25	--
28	0.0022	0.24	--
35	0.0026	0.25	1.8
Depuration 1	--	0.09	--
3	--	0.048	--
7	--	0.014	--
10	--	0.03	--
14	--	0.025	--

^aMean based on 8-10 analyses.