Meeting 3/30/77

EEE BRANCH REVIEW

DATE: IN _____ OUT _____ IN 7/15/76 OUT 10/6/76 IN _____ OUT _____

FISH & WILDLIFE ENVIRONMENTAL CHEMISTRY EFFICACY

FILE OR REG. NO. 3125-25, 193, 123, 102

PETITION OR EXP. PERMIT NO. 5F1546

DATE DIV. RECEIVED 6/29/76

DATE OF SUBMISSION 6/16/76

DATE SUBMISSION ACCEPTED 3C1D-2B-Yes

TYPE PRODUCT(S): (I,) D, H, F, N, R, S

PRODUCT MGR. NO. Sanders (12)

PRODUCT NAME(S) Guthion

COMPANY NAME Chemagro

SUBMISSION PURPOSE Amendment to add pasture grass in states east of Mississippi and for alfalfa and clover - mixed stands in states east of Miss.

CHEMICAL & FORMULATION O,O-Dimethyl S-[(4-oxo-1,2,3-benzotriazin-3(4H)-yl)methyl] phosphorodithioate

1.0 Introduction

1.1 Physical and chemical properties reviewed earlier

1.2 Percent active

EPA Reg. # 3125-193	50% ai WP
EPA Reg. # 3125-25	25% ai WP
EPA Reg. # 3125-102	22.2% ai 2L
EPA Reg. # 3125-123	22.0% ai 2S

1.3 Use on alfalfa and cloves in mixed stands with grasses east of the Mississippi River.

Use on pasture grasses east of the Mississippi River.

Use on alfalfa and clover has been registered but mixed stands and pasture grasses are not.

1.4 See previous reviews

3125-123	5/27/75
3125-25	6/9/75
Answer to letter dated 2/25/71	
3125-123, 25, 102, 123, 193	1/21/72
3125-25, 102	4/11/75
3125-123 5F1548	5/14/75
OF0984	5/5/71, 7/15/70
OF0869	10/21/70, 9/23/69
OF0539	2/1/68
OF0762	10/17/68
OF0653	10/27/67
OF0582	11/22/67
3125	5/10/66
3125-132, 167	5/27/66

2.0 Directions for Use

2.1.1 For 50 WP: Use 1/2 to 1 1/2 lbs (4 to 12 oz ai/A) per acre in 10-25 gallons of water.

2.1.2 For 25 WP: Use 1 to 3 lbs (4 to 12 oz. ai/A) per acre in 10-25 gallons of water.

2.1.3 For 2S & 2L: Use 1 to 3 pints per acre in 10-25 gallons of water.

2.2.1 For 50 WP:

Do not apply within days of harvest	Rate of application per acre
14	1/2 to 3/4 lb.
16	1 lb.
21	1 to 1 1/2 lbs.

2.2.2 For 25 WP:

Do not apply within days of harvest	Rate of application per acre
14	1 to 1 1/2 lbs.
16	2 lbs.
21	above 2 lbs.

2.2.3 For 2S & 2L:

For Alfalfa & Clover

A. Do not apply more than twice per cutting at the one pint rate for alfalfa & clover at intervals of 10 to 11 days.

B. Apply only once per cutting at rates above 1 pint per acre for alfalfa and clover.

C. Do not apply within days of harvest	Application rate per acre
14	1 to 1 1/2 pints
16	2 pints
21	above 2 pints

For pasture grasses

A. Do not apply more than once per cutting

B. Do not harvest within 16 days of application at 2 pints rate or 21 days rates above 2 pints.

3.0 Discussion of Data

This is a completeness review under 2B submission. All references are found under accession #224703 dated June 1, 1976.

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3.0.1 Below is a list of some of the papers submitted under environmental chemistry data requirements. The data presented in those papers are not environmental chemistry data so not germane.

They are submitted under accession number 224703.

Report #1217C: Action of the insecticides "Gusathion" on cotton plants; and the problem of residues in cottonseed.

Report #16176: The experimental use of Guthion as a selective fish eradicator - F.E. Meyer, Transactions of the American Fisheries Society. Vol. 94, #3, 203 (1965).

Report #16950: The effect of feeding Guthion on the blood cholinesterase activity and milk production of dairy cows, C.A. Anderson, Research and Development, Kansas City, Missouri.

Report #17889: Toxicity and fate of insecticide residue in water: E. P. Lichtenstein et al. Arch. Environ. Health - Vol. 12, 199 (1966)

Report #18636: Guthion - C^{14} study on lettuce.

Report #34933: Studies on the mechanism of Azinphosmethyl resistance in the predaceous mite. N. Motoyama et. al. Pest. Biochem. & phys., Vol. I, 205 (1971).

Report #35113: The in vitro metabolism of Azinphosmethyl by mouse liver. N. Motoyama and W. C. Deuterman. ibid. Vol. 2, #2 170(1972).

Report #35114: In vitro metabolism of Azinphosmethyl in susceptible and resistance houseflies. N. Motoyama and W.C. Deuterman. ibid, Vol. 2, 113(1972).

Report #35408: The effect of daily oral administration of Guthion to cattle at doses of 5 & 15 ppm for 30 days - C.R. Crawtford and R. M. Anderson. Chemagro R & D. Stanley Kansas.

Report #37138: Uptake and Translocation of Guthion by Beans and Barley - K. M. Al-Adil, et. al., J. Agr. Food Chem., Vol. 21, No. 3, 376 (1973).

Report #38944: Studies on the Uptake and Metabolism of Gusathion in Kidney Beans - W. Steffens and J. Wieneke, Radioagronomie Task Group, Nuclear Research Installation, Julich, West Germany.

Report #41372: The Metabolism of Guthion in Grain Sorghum Plants - R. R. Gronberg, et. al., Research and Development, Chemagro, Kansas City, Missouri

Report #44756: The Metabolism of Guthion in Oranges - R.R. Gronberg, et. al., Research and Development, Chemagro, Kansas City, Missouri

Report #45571: Influence of Humidity and Rain on Uptake and Metabolism of ^{14}C-Azinphos-Methyl in Bean Plants - W. Steffens and J. Wieneke, Archives of Environmental Contam. and Tox. Vol. 3, 364 (1975).

3.1 Hydrolysis Studies

The following hydrolysis studies are submitted under accession number 224703.

3.1.1 Report #32670: Effect of Light, Temperature, and pH on the Degradation of Azinphosmethyl - T. T. Liang and E. P. Lichtenstein, J. of Econ. Entomology, Vol. 65, No. 2, 315 (1972)

Study was carried out for 7 days in dark at 25° in buffered aqueous solutions at 2 ppm for pH 6, 7, 8, 9, 10, 11. The pesticide was relatively stable at pH 6 through 9 but decomposed at higher pH.

pH	8	9	10	11
Azinphosmethyl and N-mercaptomethyl benzazimide	87.1	59.8	18.6	0.1
N-methyl benzazimide	0.1	16.7	33.6	0.4
P = O Azinphosmethyl	1.9	12.8	29.8	1.1
Anthranilic acid	0.1	0.3	0.1	0.2

balance is unidentified metabolites.

The ^{14}C label is on the carboxyl of the 1,2,3-benzotriazin-4(3H)-one ring.

Analysis involved TLC, autoradiography, and liquid scintillation counting.

Conclusion: The higher the pH, the faster the degradation of azinphos.

The rate, half life, and material balance of hydrolysis in deionized sterile water is needed. Data for hydrolysis studies at pH 6 and 7 were done but not reported.

3.1.2 Report #41038: Guthion Half-Life in Aqueous Solutions and on Glass Surfaces - B. Heuer, et. al., Bull. of Environ. Cont. and Tox., Vol. 11, No. 6, 532 (1974)

The ^{14}C label is on the methylene group. Hydrolysis studies were carried out in buffered water and on wet and dry glass beads. ($t_{1/2}$ in days)

Temperature:	Hydrolysis in water			Dry Glass Beads	Wet Glass Beads
	pH 8.6	pH 9.6	pH 10.7		pH 9.6
6°	36.4	4.95	3.9	99	91
25°	27.9	2.40	2.0	66	10
40°	7.2	0.65	0.41	48	1

Methods of analysis were gas chromatography and liquid scintillation counting.

Conclusion:

1. We do not know if the hydrolysis is carried out in dark or not.
2. We do not know the initial conc. of Azinphos methyl in water or beads. We do not know identity and amount of hydrolysis products (material balance).
3. ^{14}C labeling was carried out on -CH2-group and not on aromatic ring as would be required.
4. Degradation of Guthion in water and on beads increased with increase of temperature and pH.
5. On dry glass beads, a lag period exists between pesticide incubation and degradation. On wet glass beads, a lag was observed at 6°C.
6. This study is not acceptable.

3.2 Photodegradation Studies: Accession number 224703

3.2.1 Report #32670: Effect of light, temperature and pH on the degradation of Azinphosmethy. E. P. Lichtenstein et. al. J. of Econ. Entomology, Vol. 65, #2,315 (1972).

UV studies in water at 2 ppm

UV (2537A°) exp. time:	0.5	1	2 hr.
Azinphosmethyl N-mercaptomethyl benzazimide	25.6	5.1	2.2
N-methyl benzazimide	2.1	3.5	3.0
Benzazimide Azophosmethyl oxygen analog	47.8	49.5	45.1
Anthranilic -	2.0	5.5	3.8

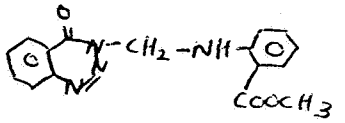
Remainder was a water soluble unidentified metabolite.

It is also observed that higher the temperature higher the metabolite N-methyl benzazamide and less azinphosmethyl. ^{14}C label was on the carboxyl of the 1,2,3-benzotriazin-4(3H)-one ring. Autoradiography is the method of analysis.

Conclusion: Half-life is less than half an hour in water. Study is carried out at 2537A° and should have been carried out at 2800A° or above or in natural sunlight. ^{14}C label should be on the aromatic ring. Material balance is needed. The study is not acceptable.

3.2.2 Report #48754: Experimental Approaches to Pesticide Photodecomposition - D. G. Crosby, Pesticide Reviews, Vol. 25, pg. 7 (1969)

Guthion likewise appeared to abstract hydrogen from its solvent in UV light (Kurihara and Crosby 1966). Irradiation in hexane solution produced benzazimid and trimethyl phosphorodithioate, together with a small amount of anthranilic acid and much cholinesterase-inhibiting polymer. However, irradiation in methanol also produced a large proportion of X and demonstrates the importance of solvent interaction during photolysis.



X

Conclusion: This study is not acceptable since no experimental details. This is a review article.

3.2.3 Report #44013: Degradation of ^{14}C Labeled Azinphos on Glass Plates as Compared to the Metabolism on Plant Leaves - J. Wieneke and W. Steffens, Arbeitsgruppe Radiogronomie der Kernfarshungs-anlaze Julich, West Germany

Degradation of ^{14}C-labeled azinphos-methyl dissolved with formulation in water under different environmental influences (light, time, temperature) Daylight: Nov. 1 - 7. C^{14} in carbonyl group.

Con. of Azinphos-methyl used was below 20 ppm.

Treatment	Days	% Radioactivity of applied Hexene	Chloro-form	Water	Rest-activity	Recovery
Dark + 23°C	3	77,1	12,5	2,9	0,2	92,7
Daylight 12 ± 7°C	3	82,5	8,6	6,1	0,1	97,3
Growth room	3	95,2	4,7	1,8	0,2	101,9
Dark + 23°C	7	91,1	3,7	3,3	0,1	98,5
Dark (+4° C)	7	92,6	4,3	0,6	0,1	97,6
Daylight 12 ± 7°C	7	54,9	18,2	16,1	0,1	89,3
Growth room	7	80,5	14,4	5,9	0,3	101,1

+ Glassware, discarded separation solution etc.

Conclusion: ^{14}C labeling was done on carbonyl group so this study is not acceptable. We need ^{14}C ring labeled study, dissipation, amounts and identity of transformation products (material balance).

3.3 Analytical Methods: Accession Number 224703

3.3.1 Report #5520: Colorimetric determination of Guthion residues in crops.

Reviewed earlier on 4/10/67 and 10/27/67 and accepted on 10/27/67

3.3.2 Report #7407: Application of the photofluorometric method developed for the determination of Guthion residues to the determination of residues of certain Benzazimide moieties of Guthion.

Reviewed earlier on 10/27/67 and accepted on 10/27/67.

3.3.3 Report #13517: A Colorimetric Method for the determination of Guthion residues in soil April 21, 1964.

Reviewed earlier and accepted on 10/27/67

3.3.4 Report #17755: Spectrophoto fluorometric method for Guthion residues in Milk and Animal tissues - J. M. Adams and C. A. Anderson, J. Agr. and Food Chem., Vol. 14, #1, 53 (1966).

Reviewed and accepted on 4/10/67.

3.3.5 Report #27835 and 27836: Determination of Dasanit, Guthion Meta-Systox-R, Nemacur and trichlorfon in soil by Thermionic emission Gas-chromatography and recovery studies.

Recoveries were 84, 91 and 106%, when applied as 1 ppm, when applied to clay loam, high organic clay loam and sandy loam respectively.

Reviewed and accepted on 11/22/67.

3.4 Frozen storage stability of Guthion, Accession Number 224703.

3.4.1 Report #48473: The Stability of Guthion in Silt Loam Soil under Frozen Storage - C. L. Close, Research and Development, Chemagro, Kansas City, Missouri

Soil Analysis

	Sand	Silt	Clay	OM	pH
Silt Loam Soil	3%	75.0%	22%	2.3	5.4

Silt loam containing ^{14}C-ring labeled Guthion fortified at 10 ppm was stored frozen (-10°C) for 93 days. Guthion was readily extracted from the soil and found to be stable under these conditions. Recovery was 100% of initial concentration with 97% as parent compound indicating complete extraction and stability under freezer conditions.

Conclusion: Guthion is stable at - 10°C for up to 93 days.

3.4.2 Report #8682: The Effect of Frozen Storage on Guthion Residues in Various Crops - C.A. Anderson, Research and Development, Kansas City, Missouri

Different fruits and vegetables were stored at 0 to -10° F and analysis were carried out at various intervals from 0 week to as high as 261 weeks.

In most cases residue was found more for longer storage than it was found for shorter periods of time.

3.5 Volatilization sutdies: Accession #224703

3.5.1 Report #48755: Volatilization of Insecticides from Various Substrates - E. P. Lichtenstein and K. P. Schulz - J. Agri. Food Chem., Vol. 18, No. 5, 814 (1970)

Physical Properties of Guthion

Vapor Pressure mm Hg	Water Solubility PPM
$< x\ 10^{-7}$	34

Initial con. of Guthion is 2.5 to 20 ppm.

Volatilization of Guthion from various substrates at 30°C volatilized in % of applied insecticide/24 hr.

	Glass Beads	Tap Water only	Soil[1]	Algae[2]	Buffer Solution pH 7.0
Liquid scintillation counting	<0.01	ND	<0.01	<0.01	0.02± 0.01
Gas liquid chromatography	ND	ND	ND	ND	--

ND = not detected
[1]Loam soil particles suspended in tap water.
[2]Algae cells suspended in nutrient media

Flasks attached to vapor traps were shaken, instead of having nitrogen pass through the soil.

Conclusion: Guthion does not volatilize readily.

3.6 Microbial Studies: Accession #224703

3.6.1 Report #35134: Effect of Guthion on microbial population. L.S. Houseworth and B.G. Tweedy, Dept. of Plant Path., Univ. of Missouri, Columbia, Missouri.

Conclusion:

1. Guthion was added to two soils La. Commerce silt loam and Indiana clay loam at 50 and 250 ppm showed no effect on soil populations of microorganism over a period of 56 days.

2. Study is not acceptable.

3. Effect of pesticide on populations of fungi, bacteria, and actinomycetes were studied. Specific microorganisms were not reported.

3.6.2 Report #46162: Microbiological Studies on the Yeast Fermenting of Red Peppers containing Guthion - S. Sanders, Frank Foods, Cincinnati, Ohio

Report says microbiological studies on the yeast fermenting red peppers and found that Guthion has no effect on the fermentation.

Conclusion: No details of any kind.

We do not require study on yeast fermentation.

3.7 Leaching studies: Accession #224703

3.7.1 Leaching studies in aged soil

Report #48466: Leaching Characteristics of Guthion on Aged Soil - S. Atwell and C. Close, Research and Development, Chemagro, Kansas City, Missouri, April 30, 1976

For soil analysis see report #48473 under frozen storage stability of Guthion.

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^{14}C ring labelled Guthion was incubated in silt loam soil at 1.0 ppm under aerobic conditions for 28 days. The column is 12" long and 1.5 cm I.D. Water was passed through the soil column each day equivalent to 0.5 inches of rainfall for 45 days. Samples were analyzed by liquid scintillation counting and TLC.

Distribution of ^{14}C after aging Guthion 28 days on silt loam soil.

	% Distribution of Activity ^{14}C
Organosoluble	
Parent Guthion	19.0
Benzazimide	5.3
Unidentified	13.7
Insoluble[1]	
Humic acid fraction	50.1
Fulvic acid fraction	10.5
Humin	1.4

[1]Bound soil residue subjected to humic/fulvic acid fractionation scheme.

Leaching of Guthion-ring-UL-^{14}C Aged in Silt Loam Soil

Soil Depth (Inches)	% of Total Activity Found
0-2	90.0
2-4	2.8
4-6	1.2
6-8	0.6
8-10	0.5
10-12	0.5
Leachate	4.4
Total:	100.0

Conclusion:

1. Guthion leaches slightly. 92.8% of the ^{14}C equivalent of Guthion was found in top 4" of soil and 94% found in top 6" of soil. Only 4.4% found in leachate with 12" long column and after 45 days with 0.5" of rain everyday for 45 days.

2. Identification of metabolites in column segment is needed.

3.7.2 Report #28936: Soil Runoff, Leaching and Adsorption and Water Stability Studies with Guthion - D. R. Flint, et. al., Research and Development, Chemagro, Kansas City, Missouri

	Soil Analysis					
Texture	% sand	% silt	% clay	% O.M.	Bulk density gm/ec	pH
Sandy loam	56.4	33.1	10.5	1.4	1.50	6.4
Silt loam	16.7	62.8	20.5	1.8	1.34	5.5
High organic Silt Loam	24.2	56.8	19.0	4.6	1.28	5.4

Runoff Studies

Run off studies were carried out on 5, 10, and 15 feet long lots with 1 inch slope per foot. Guthion was applied at 20 lb ai/A.

Recovery in runoff water collected 5 feed from the application area on sandy loam soil, was 1.51% of the applied material; all other recoveries were less than 0.8%. Residues in runoff water decreased as it traveled longer distances. Gas liquid chromatography was the method of analysis.

Adsorption Studies:

Following data obtained on adsorption:

	Kd (ml/gm)[1]
Sandy loam	3.33
Silt loam	11.04
High Organic Silt Loam	28.50

Concentration of 2.67, 3.55, and 4.44 ug/ml were used.

[1]Kd is the adsorption coefficient obtained by the batch technique.

Adsorption increased from sandy loam to silt loam to organic silt loam.

Leaching Studies:

It was carried out on three different soils used in adsorption studies. Guthion used was 10 ppm relative to soil. Column used was 45 cm long.

	R inches
Sandy Loam	62
Silt Loam	195
High Organic Silt Loam	186

R is number of inches of rainfall required to leach Guthion 12 inches into the soil.

Hydrolysis Studies

It was carried out at 25 and 50°C and in buffer and in amber bottles.

Stability of Guthion in aqueous media under various conditions

System	pH	Half life in days 30°C	50°C
pH Buffers	5	17.3	1.8
	7	10.0	1.3
	9	0.5	0.08
wide shallow vessel of pond water and silt held outdoors	7	1.2	(average temp. 29°C)

Conclusion:

1. We do not require runoff studies.

2. Guthion is highly adsorptive in soil. We do not require adsorption studies for these proposed uses.

3. Leaching study is not acceptable:

   a. We do not have identity of metabolites present in various segments of columns
   b. Study should have been carried out using ring labeled ^{14}C-Guthion
   c. Material balance is needed

4. Hydrolysis study is not acceptable

   a. No metabolites identified in the hydrolyzed products
   b. No initial conc. of Guthion is reported.
   c. No material balance
   d. Hydrolysis study using ring-labeled Guthion is preferred.

3.8 Soil Persistence: Accession #224703

3.8.1 Reports #s 17908, 17909, 17910, 17911, 19319 and 19333

Persistence study was carried out with 10 ppm incorporated 0-6" of soil. This is a field study.

Soil Type	Total Rain from application to final sampling		1. Days First Application to sampling 2. Net residue ppm					
		1.	1	32	112	182	424	
Muck-Sand	52.4 inches	2.	15.7	5.2	0.8	0.2	0.2	
Muck-Sand	52.4	2.	11.6	5.9	4.5	0.9	0.5	
		1.	0	30	93	177	202	366
Clay	48.53	2.	10.7	6.6	8.1	0.4	0.4	0.6
Clay	48.63	2.	13.9	19.9	5.1	ND	0.6	1.4
		1.	1	30	86	176	331	
Clay	36.88	2.	3.3	2.2	0.7	0.5	0.6	
		1.	1	30	64	181	371	
Clay	40.45	2.	2.1	3.1	1.3	1.0	0.5	

Conclusion:

1. Degradates have not been identified.
2. No temperature is given.
3. It appears that Guthion is persistent for at least a year.
4. No data as to how much leached below 6" of soil. This is needed because of 6" incorporation ~~soils.~~

3.8.2 Report #25186: Persistence and degradation of Azinphosmethyl in soils as affected by formulation and mode of application. K.R. Schultz, et al, J. of Economic Entomology Vol. 63, #2, 432 (1970).

This is field as well as lab studies.

In field condition parent compound was lost by 50% in 12 to 28 days. In lab studies at 20 ppm 13% of ^{14}C was recovered in form of parent compound and its metabolites. Field studies were carried out at 3 ppm.

In loam soil, Carrington silt loam and quartz-sand major metabolite was benzazimide. Mercaptomethyl benzazimide. N-methyl benzazimide and its disulfide were found in minor amounts. GLC and TLC were analysis methods.

Conclusion:

1. No soil analysis.
2. No material balance in lab studies
3. No information on bound and extractable residues
4. 50% is dissipated in 12 to 28 days.

3.8.3 Reports #27888, 27889, 27890

Soil persistence study:

5 ppm in soil incorporation

This is a field study

Soil analysis:	Sand	Silt	Clay	pH	OM
Silty Clay Loam	8%	62%	30%	6.7	3.2%

1. days to final sampling
2. ppm analysis

	Total rain from application to final					
1.	-	0	6	15	22	29
2.		5.87	1.02	2.57	0.49	-
Sandy Loam	3.46	1. same				
High organic Silt Loam	3.46	2.	9.86	5.86	6.69	1.72	2.12
silt loam	3.46	1. same				
		2 -	12.99	7.70	10.72	2.32	1.80

Conclusion:

Over 10% persistence after 30 days. No soil analysis.

3.8.4 Report #45509:

Behavior of Five Organophosphorus Pesticides in Dust Derived from Several Soil Types - Yutaka Iwata, et al., Bull. of Environ. Cont. and Tox., Vol. 14, No. 1, 49 (1975)

Soil Characteristics

Soil[a/]	Mechanical analysis, % Sand	Silt	Clay	pH	Saturation percentage	% organic matter
#58	53.6	31.0	15.4	6.9	26.3	0.8
#59	12.5	50.7	36.8	7.3	48.0	2.1
#60	22.4	34.5	43.1	7.3	57.6	2.3
#61	56.0	33.0	11.0	7.6	22.8	1.8

a/ #58 = Three Sisters Ranch, fine sandy loam. #59 = B and W Ranch, silty clay loam. #60 = Tulare, clay. #61 = Baer Ranch, sandy loam.

Recovery data for Azinphosmethyl from soil dust treated at 500 ppm

Soil[a/]	Days (ppm) 0	4	10	20	30	50	52	60	74	100	150	200
Mocho Silt Loam	420	300	200	140	80		36		22	9.8	4.2	1
Linne Clay	420	300	210	120	64		20		6.9	2.5	-	-
Madera Sandy Loam	430	410	400	350	340		290		260	190	130	72
Laveen Loamy Sand	430	420	420	370	380		290		230	180	80	39
Santa Lucia Silt Loam	450	370	320	270	230		130		55	24	9.8	5
Windy Loam	410	400	350	320	270		250		230	160	110	89
#58	450	440	410	370	330	280		220	160	100		
#59	450	400	270	170	110	46		14	4.8	-		
#60	460	330	250	130	68	26		8.5	3.0	-		
#61	460	420	340	240	200	130		78	44	21		

a/ Soil moisture, except for parathion-fortified Santa Lucia silt loam (60%) and Windy loam (70%), adjusted to 40% of maximum retentive capacity, as determined for unsieved soil.

Conclusion:

1. Study is done at 500 ppm. In practice, we are working at 1 ppm in the fields.

2. Guthion is persistent for over 10% in several soils for more than 200 days.

3.8.5 Report #44757: Persistence of Azinphosmethyl in Soil - D.C. Staiff, et al, Bull. of Environ. Cont. and Tox., Vol. 13, No. 3, 1 (1975).

Soil Analysis

	Clay	Silt	Sand	OM	pH
Sandy Loam	6.0-10.2	26.0-29.0	60.0-67.3	1.0-3.4	6.6-7.8

Each plot of 30 cm square was used and it was applied 1.89 liters of liq. Guthion regardless of its conc.

Leaching of 18.1% Liquid Emulsifiable Concentrate Azinphosmethyl Formulation in Sandy Loam Soil[a]

Sample depth (cm)	Pesticide content of soil (ppm)[b]
0 - 7.5	361.0
7.5 - 15	1054.0
15 - 22.5	62.3
22.5 - 30	3.7
30 - 37.5	0.5
37.5 - 45	nl[c]
45 - 52.5	nl[c]
52.5 - 60	nl[c]

[a]Conducted at year 8 to study effect of leaching.
[b]Average of 8 replicates
[c]Below lower limit of sensitivity of method (<0.05 ppm).

Conclusion: For the 18.1% concentration, levels of Guthion in the soil decreased to less than half of the original concentration by the end of the first year. After eight years of normal weathering, Guthion had not leached beyond 30 cm. Most of the leachate was found in the top 15 cm.

Tests to determine persistence after spillage in sandy loam soil were done with 8X (0.36%) spray solution and 1X (0.045%) spray solution.

Conclusion: At high concentrations, Guthion persists for several years.

3.8.6 Report #36693: Dissipation of Guthion, Sevin, Polgram, Phygon, and Systox from Apple Orchard Soil - R. J. Kuhr, et. al., Dept. of Ent., NYS Agric. Expt. Station, Geneva, New York

This is a field study. Guthion was applied to apple orchard soil at the rate of 0.75 ai/A on June 7, 18, 30 & July 19 of 1971. Total application was 3.0 lb ai/A. 90% of the Guthion was dissipated in 90 days.

This study is not acceptable because no soil analysis.

3.9 Sterile vs. Non Sterile Soil: Accession #224703

3.9.1 Report #14836: Recovery of Guthion from soil

Recovery studies of Guthion and its metabolites.

3.9.2 Report #40785: Kinetics of Azinphosmethyl Losses in the Soil Environment - B. Yaron, et. al., J. Agr. Food Chem., Vol. 22, No. 3, 439(1974)

Soil silty loamy loessial sierozem: pH - 8.4, O.M. = <1.0%

Half-Life (T 1/2 in days) of Azinphosmethyl in natural and sterile soils as affected by soil moisture and temp.

Temp. C°	Sterile Soil		Natural Soil	
	Dry	Wet	Dry	Wet
6	484	88	484	64
25	135	29	88	13
40	36	6	32	5

Samples were analyzed by gas chromatography.

Conclusion: Guthion is degraded faster with wet soil and high temp. than with dry soil and low temperature. Rate of degradation of Guthion is faster in natural soil compared to sterile soil.

Conclusion:

1. Degradation is microbial as well as chemical.
2. Analysis of degradation products is needed.
3. This is not an acceptable study.

3.10 Accumulation in higher animals: Accession #224703

3.10.1 Report #17756: Nature and Extent of Guthion in Milk and Tissues resulting from treated forage - L.J. Everett, et al, J. Agr. and Food Chem., Vol. 14, #1, p. 47 (1966)

Reviewed on 9/23/69 and accepted.

3.10.2 Report #17758: Extent of residues in milk resulting from use of Guthion-treated forage - W.W. Loeffler et al. J. Agr. Food Chem., Vol. 14 #1, p. 46 (1966)

Reviewed on 9/23/69 and accepted.

3.10.3 Report #32914, 32915 and 32916. Recovery of Guthion from poultry tissues and eggs.

Reviewed and accepted on 10/25/72.

3.11 Fish Accumulation Studies: Accession #224703

3.11.1 Report #48221: Accumulation and persistence of residues in Channel Catfish exposed to Guthion-^{14}C (Ring labeled), April 28, 1976.

^{14}C residues in whole bodies of channel catfish during a 28 day continuous exposure to ^{14}C-Guthion at a 15 ppb* & actual con. of ^{14}C in water

^{14}C residues in whole bodies of channel catfish during a withdrawal period following a 28-day continuous exposure to Guthion ^{14}C at a conc. of 15 ppb.*

Exposure data			Withdrawal data		
Day of exposure or withdrawal	Average Residues (ppb)	Accumulation factor	Conc. of water exposure days (ppb)	Average residues ppb	Accumulation factor
0 (1 hr)	134	13		-	-
0 (2 hr)	191	19	9.5	-	-
0 (6 hr)	331	33		206 (5 hr)	21
1	635	64	7.3	132	13
4	1385	139	16.0	93	9
7	530	53	15.9	86	9
10	688	69	17.3	71	7
14	586	59	10.6	67	7
21	542	54	16.2	68	7
28	626	63	14.5	62	6

*Base on 15 ppb exposure level

Distribution of ^{14}C is fish as follow:

	Total ^{14}C	% of Total % Guthion	% DES Methyl Guthion	Un-identified	% of whole body WA
Head, Viscera and scales	60%	60%	40%	-	68%
Edible portion	40%	42%	50%	8%	32%

Conclusion

There is low accumulation in channel catfish because rapid uptake is accompanied by rapid excretion. This study is acceptable under the old guidelines.

3.12 Rotational Crop Studies: Accession #224703

Report #48668: Guthion ^{14}C residues in field rotational crops from aged soil (Interim report) June 1, 1976

Guthion ^{14}C (ring labelled) applied at a 16 oz ai/acre (6" deep) (0.5 ppm) to clay loam soil.

Soil Analysis

	Sand	Silt	Clay	O.M.	pH
Sandy Clay Loam	69%	10%	21.0%	5.1%	6.6

Rotational crops were planted 127 days after application of Guthion. ^{14}C was counted by liquid scintillation counting.

Total ^{14}C residues in sandy clay loam soil after ^{14}C-guthion incorporation.

Days interval after addition of ^{14}C Guthion	Residues PPM Soil A	Soil B	Days Post Planting	Residues ppm Wheat Forage	Green Bean Forage	Turnip Root	Turnip Forage
0	0.8	0.6					
7	0.7	0.8					
28	0.6	0.9					
56	0.6	0.9					
120	0.5	0.5					
127	0.8		Rotational Crop planted				
141	0.5		14	0.56	0.09	-	0.23
169	0.6		42	0.32	0.09	0.30	0.10
190	0.7		63	-	-	0.04	0.06

% distribution of metabolites in Wheat Forage 28 days post planting (169 days post treatment) in ^{14}C-Guthion sandy clay loam soil.

Fraction	Metabolites		% Distribution	^{14}C PPM
Insoluble			62.3	0.20
Organic	Unknown	26.4		0.08
	Benzazimide	11.3		0.04
	Guthion	0.0		-
	Guthion-oxygen analog	0.0		-
	Sub Total	37.7		0.32

So total is 100%: Insoluble 62.3% + organic soluble 37.7%

Conclusion

1. The pesticide was found to be stable in the soil in this study.

2. Residues are taken up in crops rotated at 127 days after soil treatment and appear to decline through plant growth. Study was terminated before mature sample when taken for analysis.

3. We cannot adequately determine if residues would be present in mature rotational crops.

3.12.2 Report #89076: Guthion Residues in Broccoli - Research and Development, Chemagro, Kansas City, Missouri

3.12.3 Report #9709e: Guthion Residues in Sugar Beets - Research and Development, Chemagro, Kansas City, Missouri

Conclusion: We can't accept above two reports as rotational crop data because

1. No experimental details

2. We even can't figure out if it is residue data or rotational crop data.

3.13 Reentry Data. Accession #224703

Report #38944: Studies on the Uptake and Metabolism of Gusathion in Kidney Beans - W. Steffens and J. Wieneke, Radioagronomie Task Group, Nuclear Research Installation, Julich, West Germany

A linear decrease in concentration of free Guthion and its degradation products on the surface of kidney bean leaves with time was found. This was determined by washing the leaves with benzene and

measuring the ^{14}C content. A corresponding increase of ^{14}C in the water fraction, residue, and remainder of the plant with time was also found. Material balance was 97-98%. ^{14}C was counted by liquid scintillation spectrometry. The water phase was also analyzed by thin layer chromatography. Half-life of free guthion and its degradation products is between 28 and 42 days.

In a previous study, it was determined that light alone does not stimulate degradation of Guthion. Light in combination with water does cause degradation. Varying rates of uptake and metabolism of Guthion by plants, which are found in these studies, seem to be the result of varying sunlight and humidity. The temperature may also affect the rates. The emulsifier which was added may have increased or affected the decomposition or catabolism of Guthion on plants. The effect of the emulsifier has not been determined.

Only metabolites or degradates were incorporated into the plant. Metabolites and degradates were analyzed by thin layer chromatography, autoradiography, and liquid scintillation counting. Some of the metabolites and degradates were identified as Guthion-M-PO, benzazimide, N-hydroxy-benzazimide, di-benzazimide sulfide or disulfide, and possibly N-methyl-benzazimide.

Decomposition of Guthion on glass slides was studied under several climate chamber conditions. Guthion is very stable on glass slides under climate conditions. No emulsifier was used.

3.13.2 Report # 44013: Degradation of ^{14}C Labelled Azinphos on Glass Plates as Compared to the Metabolism on Plant Leaves - J. Wieneke and W. Steffens, Arbeitsgruppe Radioagronomie der Kernfarschungsanlaze Julich, West Germany

^{14}C label was in the carbonyl position of the ring. Liquid scintillation counting, autoradiography, thin layer and gas chromatography were analysis methods. Azinphos-methyl decomposed very slowly on glass plates in the absence of water. The rate of decomposition was faster on plant leaves because the plant tissue metabolizes azinphos-methyl.

Influence of humidity and rain on uptake and metabolism of ^{14}C-azinphos in bean plants. W. Steffens and J. Wieneke, Arbeitsgruppe Radioagronomie der Kernforschungsanlage Julich.

Carbonyl-^{14}C-azinphos was used. Low humidity and dry periods will cause azinphos-methyl to be relatively persistent on the leaf surface.

3.13.3 Report #44756: The Metabolism of Guthion in Oranges. R.R. Gronberg, et al, Research and Development, Chemagro, Kansas City, Missouri

Guthion-carbonyl-^{14}C was applied to oranges under field conditions. After 7 days only 5.6%of the ^{14}C was found in the benzene rinse of the orange. Thin layer chromatography showed that the benzene rinse contained only Guthion.

3.14 Report #1584: Metabolism of P^{32}-Guthion in the White Mouse and Cockroach - R.B. March, et al, University of California, Citrus Expt. Station, Riverside, California.

74% of the Guthion and its metabolites was excreted by mice in 199 hours.

3.15 Report #17756: Nature and Extent of Guthion Residues in Milk and Tissues Resulting from Treated Forage - L. J. Everett, et al, J. Agr. and Food Chem., Vol. 14, No. 1, p. 47 (1966).

38% P^{32} Guthion was excreted in the urine and 8% in the feces of cattle in 30 hours. The residue in milk from feeding forage containing 2 ppm of Guthion will be 0.008 ppm. These residues consist of four unidentified phosphorus-free metabolites which still contain the benzazimide moiety.

3.16 Report #17758: Extent of Residues in Milk Resulting from Use of Guthion Treated Forage - W. W. Loeffer, J. Agr. Food Chem., Vol. 14, No. 1, p. 46 (1966)

While no Guthion was found in the milk, metabolites consisting of the oxygen analog of Guthion and/or other benzazimide containing moieties were present in amounts proportional to the amount fed to cows.

3.17 Report #32915: Guthion Residues in Poultry Eggs - Research and Development, Chemagro, Kansas City, Missouri

Net residue in eggs of chicken fed 0.5 to 7.0 ppm Guthion was 0.019 ppm or less.

3.18 Report #32916: Guthion Residues in Poultry Tissues - Research and Development, Chemagro, Kansas City, Missouri

Net residue in poultry tissues for 0.5 ppm in feed ranged from less than 0.01 ppm to 0.18 ppm.

4.0 Summary

4.1 Hydrolysis Studies:

A. Report #32670: Data for hydrolysis studies needed at pH 5 (or 6) & 7. Studies were done at pH 6 and 7 but data were not reported. Rate, half-life, and material balance is needed.

B. Report #41038

1. We do not know if this hydrolysis is carried out in dark or not.

2. We do not know the initial conc. of Azinphosmethyl in water or beads.

3. ^{14}C labeling was carried out on -CH2 group and not on ring as required.

4. We need material balance.

5. Hydrolysis is faster on a wet substance at higher temperature.

4.2 Photodegradation

A. Report #32760: Study has been carried out at 2537A°. It should be carried out at 2800A or above which is equivalent to sunlight or in natural sunlight. Material balance is needed. Half-life is less than 1/2 hr.

b. Report #48754: This study is a review article and no experimental details so not acceptable.

C. Report #44013: ^{14}C labeling was carried out on carbonyl group and not on ring so it is not acceptable.

4.3 Microbial studies: Effect on microbes.

A. Report #35134: Effect of pesticides on specific typical micro-organisms must be reported. Guthion did not affect micro-organism populations.

4.4 Leaching Studies

A. Report #48466: Aged leaching studies. Identification of metabolites in column segment is needed. Guthion leaches slightly.

B. Report #28936:

1. Runoff study is acceptable but is no more required.

2. Adsorption study is acceptable but is not required for these proposed uses.

3. Leaching study is not acceptable:

a. Identity of metabolites is needed.
b. Study should have been carried out using ^{14}C ring labeled Guthion.
c. Material balance is needed.

4. a. No metabolites identified in the hydrolysis products.

b. No initial conc. of Guthion is reported.

c. No material balance.

4.5 Soil Studies:

Reports #17908, 17909, 17910, 17911, 19319, and 19333.

A. Study should be carried on silt loam and clay loam soils.

B. No information on 50% and 90% dissipation time requirements.

C. Metabolites are not defined.

D. No temperature is given.

E. Guthion is persistent for at least a year.

Report #25186:

1. We need soil analysis

2. No material balance in lab studies

3. No information on bound and extractable residues.

4. 50% of the Guthion is dissipated in 12 to 28 days.

Reports #27888, 27889, and 27890

1. We need soil analysis.

2. Over 10% persists after 30 days.

Reports #45509:

Over 10% of the Guthion persists for more than 200 days.

Report #36593:

We need soil analysis.

Report #40785:

Degradation is microbial as well as chemical. Analysis of degradation products is needed.

4.6 Rotational Crop Residues studies:

Report #48668:

1. Analysis is not carried out on mature plants. We need separate analysis on wheat grain and forage.

Reports #8907b and 9709e.

1. No experimental details

2. We even can't figure out if this is residue data or rotational crop data.

4.7 Guthion does not volatilize readily.

4.8 Fish show low accumulation as a result of rapid uptake and rapid excretion. This was a catfish study with no soil. It is acceptable under old procedure but not the new guidelines.

4.9 Halflife of free Guthion and its degradation products on kidney bean leaves is between 28 and 42 days.

5.0 Recommendations

5.1 We do not concur with the proposed uses.

5.2 Following deficiencies are noted for the references submitted.

5.2.1 Hydrolysis studies

a. Report #32670: Data for hydrolysis studies needed at pH 5 (or 6) and 7. Rate, half-life, and material balance is needed.

b. Report #41038

1. We do not know if this hydrolysis is carried out in dark or not.

2. We do not know the initial concentration of Azinphos-methyl in water or on beads.

3. ^{14}C labeling was on -CH2 group and not on ring ^{14}C as required. We need studies with ^{14}C-ring labeled Guthion.

4. We need material balance.

5.2.2 Photodegradation:

A. Report #32760: Studies have been carried out at 2537A°. It should be carried out at 2800A° or above which is equivalent to sunlight or in natural sunlight. Material balance is needed.

B. Report #48754: This study is a review article and no experimental details so not acceptable.

C. Report #44013: ^{14}C labeling is on carbonyl group and not on ring as required so not acceptable.

5.2.3 Microbial studies: Effect on microbes:

A. Report #35134: Effect on specific, typical microorganisms must be determined.

5.2.4 Leaching studies

Not needed 3/30/77

a. Report #48466: Aged leaching studies. Identification of metabolites in column segment is needed.

b. Report #28936: Leaching studies is not acceptable for the following deficiencies.

1. Identification of metabolites is needed.

2. Study should have been carried out using ^{14}C ring labeled metabolites.

3. Material balance is needed.

c. Report #28936: Hydrolysis studies

1. No metabolites identified in hydrolysis studies.

2. We do not know the initial concentration of metabolites.

3. We have material balance.

5.2.5 Soil studies: Field studies:

A. Reports #17908, 17909, 17910, 17911, 19319 and 19333.

1. We do not know the time it takes to dissipate 50% and 90% of the initial concentration

2. Metabolites are not defined.

3. No temperature is given.

4. Studies on silt loam and clay loam are needed.

B. Report #25186

1. We need soil analysis.

2. No material balance in lab studies.

3. We need information on bound as well as extractable residues.

C. Reports 27888, 27889, 27890, 36593

We need complete soil analysis on above reports.

D. Report 40785: Analysis of degradation products is needed.

5.2.6 Rotational crop residue studies:

1. Report #48668: Analysis is not carried out on mature plants. We need separate analysis on wheat grain and forage.

This was a lab study.

2. We need an explanation of why the pesticide was stable in soil in this study and not in other soil studies.

3. The study is not complete enough to determine if residues are taken up by rotational crops because of the following:

   A. There is not enough sampling to predict decline curves.

   B. There is no analysis on mature crops.

Reports #8907b and 9709e - Residue data on target crops after soil application.

No experimental details. We even can't figure out if this is residue data or rotational crop data.

RE Jey 10/15/76

Ronald E. Mey, Jr. 10/6/76

Nancy Dodd

Nancy Dodd

Bipin C. Gandhi
Environmental Chemistry Section
Efficacy and Ecological Effects Branch