

AZINPHOSMETHYL

Final Report

**Task 2: Environmental Fate and
Exposure Assessment**

Contract No. 68-01-6679

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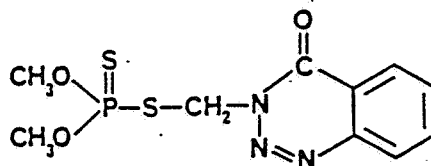
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Environmental Fate and Exposure Assessment

Azinphosmethyl

BAY 17147, CARFENE, COTNION-METHYL,
CRYSTHYON 2L, GUSATHION M, GUTHION



0,0-Dimethyl S-[(4-oxo-1,2,3-benzotriazin-
3(4H)-yl)methyl]phosphorodithioate

Azinphosmethyl is an insecticide/acaricide/molluscicide registered for use on a variety of terrestrial food crop (field, vegetable, fruit, and nut), terrestrial nonfood crop (tobacco, ornamentals, forest, and shade trees), and tree nurseries (Christmas trees). The data requirements for forestry uses may be waived if the forest use is removed from the label or if the use is defined as referring to tree plantations that are not truly forest environments. Of the total amount of azinphosmethyl applied in the United States during 1985, 34, 23.8, 6.8, and 6.8% were used on cotton, apples, peaches, and almonds, respectively. Application rates range from 0.125 to 2.4 lb ai/A. Azinphosmethyl may be formulated with endrin, ethylene dichloride, methyl parathion, parathion, captan, sulfur, ferbam, and zineb. Single active ingredient formulations consist of 2 and 3% D; 5-10% G; 25-62.5% WP; 1-2 lb/gal and 12.37% EC; 2 and 3 lb/gal FlC; and 12.4% SC/L. Azinphosmethyl is foliarly applied by ground equipment or aircraft. All liquids with a concentration >13.5% azinphosmethyl are Restricted Use Pesticides and applicators must be certified or under the direct supervision of applicators certified to apply these azinphosmethyl formulations.

The following data were submitted by Mobay Chemical Corporation under Accession Nos. 224703 (reviewed by EPA), and 099214 and 099216 (reviewed by Enviro Control, Inc., Task 1R: Review of Guthion dated July 7, 1980).

Citations found in the references but not found in the text refer to either analytical methodologies or studies considered to be scientifically invalid.

Hydrolysis Study - Report No. 67983

Hydrolysis of Guthion-ring-UL-¹⁴C was studied in sterile, aqueous, phosphate buffers at three pHs (4, 7, 9), two temperatures (30, 40°C), and two concentrations (1, 10 ppm). Half-life of Guthion at 30°C and pH 4, 7, and 9 was 40, 24, and 2 days, respectively. At 40°C and pH 4, 7, and 9, half-life was 19, 11, and 1 day, respectively. No volatile degradation products were found. Benzazimide and/or hydroxymethyl benzazimide were identified as the major degradation products in each system. Mercaptomethyl benzazimide, bis-(benzazimide-N-methyl) sulfide, and water-soluble metabolites were also found, but not greater than 10% of the total activity. The hydrolysis data requirement has been satisfied.

Photodegradation - Report Nos. 67979 and 67980

The photodegradation of azinphosmethyl-ring-UL-¹⁴C was studied (Report # 67980) in aqueous solution exposed to a high intensity mercury lamp (200 watt, 284 nm).

The half-life of azinphosmethyl was 9.4 hours in aqueous solution. ←

Benzazimide and/or hydroxymethyl benzazimide, Guthion, anthranilic acid, and methyl benzazimide were about 39, 19, 10, and 2%, respectively, of the activity in solution after 48 hours of exposure.

Photodegradation on soils (Report # 67979) was for 10 days of irradiation with a high intensity mercury lamp (200, 284 nm). The half-life was 9.1 days. ✓

The major photoproducts were benzazimide and/or hydroxymethyl benzazimide (4%), Guthion oxygen analog (3%), methyl benzazimide (1%), and bis-(benzazimide-N-methyl) sulfide (1%).

Since the light source did not simulate sunlight, the aqueous and soil photolysis studies are not satisfactory and must be repeated.

Aerobic and Anaerobic Soil Metabolism - Report No. 68030.

The metabolism of azinphosmethyl-ring-UL- ^{14}C at 2 ppm was studied in sandy soil (1.4% OM) under aerobic, anaerobic, and sterile conditions. Under aerobic conditions, azinphosmethyl half-life was 21 days. Under anaerobic conditions, following 30 days incubation in aerobic soil, the half-life was 68 days. In sterile soil, the half-life was 355 days.

Under aerobic conditions, metabolites detected were Guthion oxygen analog residues and mercaptomethyl benzazimide, benzazimide, and/or hydroxymethyl benzazimide, and bis-methyl benzazimide sulfide.

The aerobic and anaerobic soil metabolism data requirements are satisfied.

Leaching - Report Nos. 48466 and 51016

A leaching study (Report # 51016), using six soil types and soil thin-layer chromatography (TLC), showed that azinphosmethyl is in Class 2 (low mobility, Helling classification of pesticide soil mobility). Azinphosmethyl was most mobile in silty clay soil (R_f 0.24) and least mobile in sandy clay loam soil (R_f 0.11). This low mobility correlates to the relatively high adsorption of azinphosmethyl on soils.

^{14}C -Labeled azinphosmethyl was used to treat silt loam soil that was aged in a soil column and leached with the equivalent of 14 acre inches of water over 45 days. The leachate contained 4.4% of applied activity, 12.1% of which was organosoluble (did not contain azinphosmethyl). The top 2 inches contained 90% of the applied activity. The soil TLC and column leaching studies do not indicate there is a potential for leaching of azinphosmethyl to groundwater.

The leaching data requirement is satisfied.

Adsorption/Desorption - Report No. 66848

Adsorption of ^{14}C -azinphosmethyl-UL-ring from aqueous solution by sandy loam, silt loam, and silty clay soils was studied over four concentrations ranging between 0.13 to 13 ppm. The amount of azinphosmethyl adsorbed ranged from 52 to 89%. Freundlich adsorption constants (K) for sandy loam, silt loam, and silty clay soils were 7.6, 16.75, and 9.85, respectively. Total azinphosmethyl residues desorbed from soil ranged from 32 to 68%.

The leaching data requirement is satisfied.

Soil Field Dissipation - Report Nos. 67803, 67805-7, 67809-10

Soil field dissipation of Guthion (azinphosmethyl at 4 lb ai/A) was studied in four soil types: sandy loams (2.5 and 2.3% OM), sandy clay loams (2.4 and 2.6% OM), silt loam (muck, 49% OM), and sand (0.8% OM). For sandy loam soils, sampling was done at 0-6 inches and 6-12 inches at 0, 30, 58 days after application. The lowest detectable residues at 0-6 inches were 0.01 and 0.02 ppm at 30 days; at 6-12 inches, the lowest level was 0.01 and 0.04 ppm at 0 time.

For sandy clay loam soils, sampling was at 0-6 and 6-12 inches on 0, 30, 60, 119, 181, and 273 days after application. The lowest detectable residues at 0-6 inch samples were 0.01 and 0.03 ppm at 119 days; similarly at 6-12 inches, the lowest residues detected were 0.02 ppm at 30 days and 0.01 at 60 days. Half-lives of azinphosmethyl for both soils were less than 30 days (97 and >90% degraded within 30 days). Azinphosmethyl oxygen analog residues were <0.01 ppm in all samples for both soils.

For the silt loam soil, sampling was at 0-6 and 6-12 inches on 0, 30, 60, and 273 days after application. The lowest detectable residues were at 30 days (0.05 ppm) for 0-6 inches; and at 0 day (0.02 ppm) for 6-12 inches.

For the sandy soil, sampling was at 0-6 and 6-12 inches on 0, 30, 120, and 273 days after application. The lowest detectable residues were at 30 days (0.03 ppm) at 0-6 inches and at 0 day (0.04 ppm) at 6-12 inches.

In all the 4 soils tested, the field dissipation of azinphosmethyl (Guthion) was shown to be fairly rapid.

Although sampling was not done to sufficient depths to define the extent of leaching, the lab leaching studies indicate low leaching potential.

The field dissipation data requirement is satisfied.

Rotational Crops - Report Nos. 67116-67179 and 67271

At maturity, grain, vegetable, and root rotational crops planted in field plots treated with Guthion were analyzed by colorimetric and GC techniques for azinphosmethyl and its oxygen analog residues. Rates equal to 1, 2, 4, and 8 lb ai/A of azinphosmethyl were used. Maximum label rate is 4 lb ai/A per year. Crops representative of grain, pod-vegetable, leafy-vegetable, and root crop groups were planted 30, 60, 90, and 120 days after application. Results showed no residues (<0.1 ppm) of azinphosmethyl or its oxygen analog were detected in grain, pod-vegetable, or leafy-vegetable crops planted 30 days post application.

Root crops showed significant residues of 2.18 ppm at 30 days post application of 1 lb ai/A and residues of 0.72 ppm at 90 days post application of 1 lb ai/A. No residues (<0.1 ppm) were found in root crops 120 days post application of maximum label dose of 4 lb ai/A. However, at rate of 8 lb ai/A, residues of 0.53 ppm and 0.55 ppm were found at 90 and 120 days, respectively. The residues are considered to be the phenyltriazine moiety. It was detected by colorimetric, but not GC techniques. This moiety is not part of the tolerance expression in plants.

In the absence of a radiolabeled (confined) rotational crop study, it is not know if azinphosmethyl and its oxygen analogs are the only residues in the rotated crops. Therefore, the rotational crop data requirement is not satisfied and no rotational interval can be recommended.

Fish Accumulation - Report No. 48221

This is a channel catfish study in which fish were continuously exposed to ^{14}C -Guthion (ring-labeled) at 15 ppb in the absence of soil. Exposure was for 28 days, with maximum wholefish bioaccumulation (139X) at day 4. Through days 7-28 the average wholefish accumulation was 60X. During the 14-day depuration period, about 90% of the residues were released.

The fish accumulation data requirement is satisfied.

Forestry Use

The data requirements for forestry use are data gaps. These are three studies not included in the field and vegetable uses (terrestrial food crop) and are:

1. Anaerobic aquatic metabolism (§ 161-3)
2. Forest field dissipation (§ 164-3)
3. Aquatic nontarget accumulation (§ 165-5)

These studies may be waived if forest use is removed from the label or if the use is defined as referring to tree plantations that are not forest environments.

Applicator Exposure

Because of the high dermal toxicity of Guthion, we recommend that a data call-in for glove permeability information as described in ASTM 739-81-Standard Test Method for Resistance of Protective Materials To Permeation By Hazardous Liquid Chemicals be required by the Agency for Guthion EC liquid formulations. We also request that the significant carrier solvents, e.g., petroleum distillates, be included in the permeation testing. If pertinent data are not available and testing is conducted, then a protocol should be submitted to HED (Protective Clothing Work Group) for approval prior to any testing. Data on Guthion EC are not available to the Agency detailing the permeability and breakthrough times of materials used in "protective" gloves.

Reentry Interval

Currently, a 24-hour federal reentry interval has been established for all crops. California has established reentry intervals of 30, 14, 21, and 14 days for citrus, peaches and nectarines, grapes, and apples, respectively.

Guthion Poisoning Statistics

Acute hazards to Guthion (azinphosmethyl) can be measured by counting or estimating the number of deaths, hospitalizations, and visits to physicians outside of hospitals.

Mortality

During four years (1961, 1969, 1973, 1974), when all accidental deaths due to pesticides in the U.S. were counted, Guthion was found to cause, on average, 0.5 deaths per year during the four years surveyed.

Hospitalized Poisonings

Based on a 12% sample of the nation's hospitals, Guthion was estimated to have caused an average of 4 hospitalizations each year during the time period 1971 through 1976, accounting for 0.001 % of the total pesticide poisonings. This estimate is based on 3 observed cases: one occupationally related; one nonoccupational; and one intentional (suicide homicide attempt).

Physician-treated Poisoning

Based on data obtained from California (the only state which enforces mandatory reporting of occupational pesticide incidents), physicians treated an average of 5 Guthion poisonings each year from 1981 through 1985. An additional one case per year was reported as either due to shin or eye injury.

Poisonings per Pounds Used

The number of hospitalized poisonings (average per year, 1971-1976) per

million pounds reported use in agriculture, government, and industry in 1974 was 0.6. The average hospitalized poisonings per million pounds used for all pesticides was 3.4. The number of California physician-treated occupational poisonings (average per year, 1981-1985) per million pounds reported sold in California in 1982 was 9.7. On average, for all pesticides we find 1.3 poisonings per million pounds sold per year in California.

Exposure Assessment

A review of the poisoning incidence data suggests that guthion can be used safely when handled properly; however, being a Toxicity I category pesticide it can and does produce serious systemic poisoning from acute exposure. Proposed labeling language regarding worker safety is part of this standard.

The dosage of guthion received during mixing/loading and applying guthion by airblast to orchard crops is estimated to be 0.058 to 0.14 mg/kg/day. These estimates assume open pouring and the use of protective gloves and at least cotton coveralls over a shirt and pants.

The dosage of guthion received by mixer/loaders involved with aerial application of guthion to the maximum acreage treatable in a day is: 1) 0.42 to 5.1 mg/kg/day for open pouring with liquid formulations; 2) 0.011 to 0.12 mg/kg/day for liquid formulations with closed systems; and 3) 0.021 to 0.24 mg/kg/day for wettable powders with open pouring.

The mixer/loader estimates assume 30% dermal absorption and the use of protective gloves only.

Label Restrictions

All liquids with a concentration greater than 13.5% are Restricted Use Pesticides.

Treated areas should not be reentered for at least 24-hours unless protective clothing is worn.

Fields treated with azinphosmethyl may not be planted to crops other than those on the label.

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TABLE A
GENERIC DATA REQUIREMENTS FOR CHEMICAL Guthion (Azinphosmethyl)

Data Requirement	Composition	1/ Use 2/ Pattern	Does EPA Have Data To Satisfy This Requirement? (Yes, No or Partially)	Bibliographic Citation	Must Additional Data Be Submitted Under FIFRA Section 3(c)(2)(B)?3/
<u>\$158.130 Environmental Fate</u>					
<u>DEGRADATION STUDIES-LAB:</u>					
161-1 - Hydrolysis	TCAI or PAIRA	A, B, G	Yes	00029899	No
<u>Photodegradation</u>					
161-2 - In water	TCAI or PAIRA	A, B, G	No		Yes
161-3 - On soil	TCAI or PAIRA	A, G	No		Yes
161-4 - In Air	TCAI or PAIRA	A	4/		
<u>METABOLISM STUDIES-LAB:</u>					
162-1 - Aerobic Soil	TCAI or PAIRA	A, B, G	Yes	00029900	No
162-2 - Anaerobic Soil	TCAI or PAIRA	A	Yes	00029900	No
162-3 - Anaerobic Aquatic	TCAI or PAIRA	G	No		Yes/8
162-4 - Aerobic Aquatic	TCAI or PAIRA				
<u>MOBILITY STUDIES:</u>					
163-1 - Leaching and Adsorption/Desorption	TCAI or PAIRA	A, B, G	Yes	00029885 00029887	No
163-2 - Volatility (Lab)	TEP	A	4/		
163-3 - Volatility (Field)	TEP	A	4/		

- 1/ Composition: TCAI = Technical grade of the active ingredient; PAIRA = Pure active ingredient, radiolabelled;
TEP = Typical end-use product.
2/ The use patterns are coded as follows: A=Terrestrial, Food Crop; B=Terrestrial, Non-Food; C=Aquatic, Food Crop;
D=Aquatic, Non-Food; E=Greenhouse, Food Crop; F=Greenhouse, Non-Food; G=Forestry; H=Domestic Outdoor; I=Indoor.
3/ Data must be submitted no later than _____.
4/ May be needed pending Toxicology and reentry considerations.

TABLE A
GENERIC DATA REQUIREMENTS FOR CHEMICAL

Data Requirement	Composition	1/ Use 2/ Pattern	Does EPA Have Data To Satisfy This Requirement? (Yes, No or Partially)	Bibliographic Citation	Must Additional Data Be Submitted Under FIFRA Section 3(c)(2)(B)?3/
\$158.130 Environmental Fate (continued)					
<u>DISSIPATION STUDIES-FIELD:</u>					
164-1 - Soil	TEP	A,B	Yes	Acc. # 099216 Report #'s 67803, 67805-7, 67809-10	No
164-2 - Aquatic (Sediment)	TEP				
164-3 - Forestry	TEP	G	No		Yes/8
164-4 - Combination and Tank Mixes					
164-5 - Soil, Long-term	TEP	A,B	5/		No
<u>ACCUMULATION STUDIES:</u>					
165-1 - Rotational Crops (Confined)	PAIRA	A	No		Yes
165-2 - Rotational Crops (Field)	TEP	A	No		6/
165-3 - Irrigated Crops	TEP	A	7/		
165-4 - In Fish	TCAL or PAIRA	A,B,G	Yes	Acc. # 224703 Report # 48221	No
165-5 - In Aquatic Non-Target Organisms	TEP	G	No		Yes/8

5/ The low persistence of azinphosmethyl, as shown by 164-1, precludes need for this study.

6/ Additional data may be needed depending on results of the confined (165-1) study.

7/ Data will not be needed if the label contains a statement prohibiting use of water leaving treated fields for purposes of irrigating other crops.

8/ Forestry use data may be waived if forest use is removed from label, or if the use is defined as referring to tree plantations that are not truly forest environments.

TABLE A
GENERIC DATA REQUIREMENTS FOR CHEMICAL Guthion (Azinphosmethyl)

Data Requirement	Composition	1/ Use 2/ Pattern	Does EPA Have Data To Satisfy This Requirement? (Yes, No or Partially)	Bibliographic Citation	Must Additional Data Be Submitted Under FIFRA Section 3(c)(2)(B)? ^{3/}
158.130 Environmental Fate (continued)					
Subpart K Re-entry					
132-1 Foliar Dissipation	TEP	A	No	-	Yes/27 months
132-1 Soil Dissipation	TEP	A	No	-	Yes/27 months
133-3 Dermal Exposure	TEP	A	No	-	Yes/9 months
133-4 Inhalation Exposure	TEP	A	No	-	Yes