DP BARCODE : D168246

PC Code No.: 58001

Date Out of EFGWB: JAN 2 1992

TO: Larry Schnaubelt/Robert Richards
Product Manager #72
Registration Division (H7505C)

FROM: Akiva D. Abramovitch, Section Head
Environmental Chemistry Review Section #3
Environmental Fate and Ground Water Branch/EFED (H7507C)

THRU: Henry M. Jacoby, Chief
Environmental Fate and Ground Water Branch/EFED (H7507C)

Attached, please find the EFGWB review of:

Reg./File #: - Not provided-

Common Name: Azinphos-Methyl

Chemical Name: O,O'-Dimethyl-S-[(4-oxo-1,2,3-benzotriazin-3(4H)-yl)-methyl]phosphorodithioate

Type product: Insecticide/Acaricide/Molluscicide

Product Name: GUTHION

Company Name: Mobay Corporation, Agricultural Chemical Division

Purpose: Review of Accumulation in Confined Rotational Crops (165-1; MRID #413936601); Update of Status of Data Requirements.

Date Received: 2/21/90 EFGWB #: 91-0915

Action Code: 627 Total Reviewing Time (decimal days): 2.0

Deferrals to: _____ Ecological Effects Branch, EFED

_____ Science Integration & Policy Staff, EFED

_____ Non-Dietary Exposure Branch, HED

_____ Dietary Exposure Branch, HED

_____ Toxicology Branch I , HED

_____ Toxicology Branch II, HED

1. CHEMICAL:

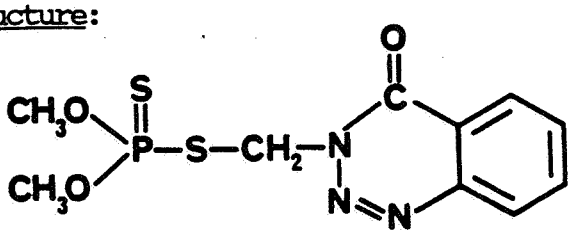
Common Name: Azinphos-Methyl

Chemical Name: O,O'-Dimethyl-S-[(4-oxo-1,2,3-benzotriazin-3(4H)-yl-methyl]phosphorodithioate

Trade Name: GUTHION

Chemical Abstracts Registry #: 86-50-0

Chemical Structure:



Physical/Chemical Properties of Active Ingredient:
Physical state and color: Cream to beige granular material
Melting point: 67-70 C
Specific gravity: 0.971 (20-25 C)
Solubility (25 C)

Water (pH 7.02)	25.1 mg/L
Acetone	80.5 g/100 mL
Toluene	40.1 g/100 mL
Methanol	3.0 g/100 mL
Heptane	0.243 g/100 mL
n-Octanol	1.17 g/100 mL
Carbon Tetrachloride	11.09 g/100 mL

Vapor pressure: $< 10^{-5}$ mmHg (testing in progress to determine exact value)
Ocatonol/water partition coefficient (K_{ow}): 543 at 25 C, pH 6.31

2. STUDY/ACTION TYPE:

Review of Accumulation in Confined Rotational Crops Study (165-1); Update status of environmental fate data requirements.

3. STUDY IDENTIFICATION:

Chopade, H.M. and Bosnak, L.L. 1990. [Phenyl-UL-^{14}C] Azinphos-Methyl Rotational Crop Study. Mobay Project ID #GU05P01; Mobay Report #99849; Completed 2/14/90. Performed and submitted by Mobay Corporation.

4. REVIEWED BY:
Silvia C. Termes, Chemist
Review Section #3
OPP/EFED/EFGWB

Signature: _____

Date: December 19 1991

5. APPROVED BY:

Akiva D. Abramovitch, Ph.D.
Section Head, Review Section #3
OPP/EFED/EFGWB

Signature: Akiva Abramovitch

Date: JAN 2 1992

6. CONCLUSIONS:

The reviewed study (#41393601) is not acceptable at this time because the length of freezer storage and storage stability data were not provided for the residues in crop and soil samples.

The study may be acceptable (and thus may fulfill 165-1 data requirements) if the registrant submits satisfactory data showing that ^{14}C-azinphos-methyl and its degradates are stable in soil and crop tissues when frozen and stored for the maximum period of time prior to analysis used in the study. The length(s) of freezer storage for soil and crop samples must be provided.

The registrant must clarify the HPLC limits of detection for parent and degradates. Identification of residues in soil at each rotation time must also be submitted.

In addition, the registrant must clarify the discrepancy noted between an earlier field study (Accesion #099214; Mobay Report 67116-67179 and 67271; reviewed by the Branch on 11/20/80 under "EFGWB #s 384/-5/-6), in which significant residues of parent azinphos-methyl and its oxygen analog were reported for the 30- and 90-day rotations (application rate 1 lb ai/A) as opposed to no parent and/or oxygen analog(s) reported at any of the three rotations included in the study conducted at an application rate of 12 lb ai/A (MRID #41393601; This review).

According to the results presented in study MRID #41393601, only metabolites containing the benzazimide moiety (detected by ^{14}C-labeling the phenyl ring) are present in the crops and soils. It should be pointed out that all of these metabolites involve cleavage of the -P-S-C- bridge of the parent azinphos-methyl either at the P-S or S-C bond. Thus, formation of species containing an organophosphate moiety (O,O'-dimethylphosphate, O,O'-dimethylthiophosphate, O,O'-dimethyldithiophosphate or other) would be expected. However, because this part of the parent was not radiolabelled it is not possible to conclude at this time if any organophosphate moiety (formed by cleavage of the -P-S-C- bridge) accumulated in the crops and/or were present in soils. Therefore, the registrant is requested to address this issue and indicate if attempts have been made to follow the fate of the organophosphate moiety in soils, crops, etc. in other studies. Instead of radiolabelling, it may have been possible to use ^{31}P-NMR to identify any of the P-containing species that may form as a result of the -P-S-C- bridge cleavage. Phosphorous-31 has a 100% natural abundance, a nuclear spin (I)= 1/2 h/2ii, and a relative sensitivity for equal number of nuclei of 6.63×10^{-2} (at constant field) or 0.405 (at constant frequency).

SUMMARY OF REPORTED DATA

^{14}C-Azinphos-Methyl residues (applied to sandy loam soil at a nominal rate of 12 lb ai/A as a 2L emulsifiable concentrate) accumulated in kale, red beets, and wheat planted at 30, 135, and 272 days post-treatment.

At the first rotation (30 days), the total residues in soil averaged 6.15 ppm. Residues in crops ranged from 0.18 ppm (beet roots) up to 9.84 ppm in mature wheat straw (1.95 ppm in mature wheat heads). Kale contained 0.62 ppm total residues (harvest 70-days post-treatment).

At the second rotation (135 days), the total residues in soil averaged 4.61 ppm in the soil. Residues in crops ranged from 0.1 ppm in beet roots to 1.68 ppm in mature wheat straw (0.27 ppm in mature wheat heads). Kale (harvest 181- day post-treatment) contained 0.27 ppm total residues.

At the third rotation (273 days) the total residues in soil averaged 3.74 ppm. Residues in crops ranged from 0.25 ppm in beet roots (1.13 ppm in beet tops) to 2.41 ppm in wheat straw (0.81 in wheat heads). Kale (harvested 322 days posttreatment) contained 0.28 ppm total residues. Note that the total residues in wheat and beets where higher in the third rotation than in the second.

Extractability (acetonitrile/HCl) of residues from soils decreased with time, with residues becoming more bound to soil as time passed. The "zero-day" extract consisted of ca. 95% parent azinphos-methyl; past 181 days, negligible amounts of changed parent (<0.1% or 0.04 ppm) were found. After 360 days posttreatment, the major metabolites were identified in soil were:

Methylsulfinylmethylbenzazimide (Me-Thio-MeBzaz-SO).....	0.80 ppm
Methylsulfonylmethylbenzazimide (Me-Thio-MeBzaz-SO_2).....	0.48 ppm
Anthranilic Acid (2-Aminobenzoic Acid).....	0.78 ppm

Minor metabolites (0.01 to 0.13 ppm): Benzazimide (Bzaz); Methylbenzazimide (MeBzaz); Benzamide

The metabolites identified in crops were all derivatives of benzazimide (that is, all of them contined a benzazimide moiety). Six of these metabolites were identified,

Cysteinylmethylbenzazimide-SO (Cys-MeBzaz-SO); Me-Thio-MeBzaz-SO; Me-Thio-MeBzaz-SO_2; Anthranilic Acid; Anthranilamide.

Cys-MeBzaz-SO was present in all crops in the first and third rotations and was detected at a maximum of 3.35 ppm in mature wheat straw of

4/

the first rotation. Me-ThioBzaz-SO and -SO_2 were also present in all crops of the first and third rotation.

According to the results reported by the authors, there were no identified metabolite that contained the intact tri-ester organophosphate moiety (parent and/or oxygen analogs or related species), which may be of potential concern as cholinesterase inhibitors.

AZINPHOS-METHYL- Environmental Fate and Transport Assessment

Based on data currently available in EFGWB files, a preliminary environmental fate and transport assessment for AZINPHOS-METHYL has been prepared (see APPENDIX).

7. RECOMMENDATIONS:

A. The registrant must provide the additional information requested in the CONCLUSIONS section, which include,

a. Storage stability data/length of freezer stability to support results of MRID #41393601.

b. Provide HPLC limits of detection for parent/degradates in crops and soil.

c. Identification of residues at each rotation time.

d. Explain the discrepancy on metabolites found in an earlier study and the new study.

e. Address the formation of species containing an organophosphate moiety and their fate/transport/accumulation.

B. The registrant should be informed of the present status of environmental fate data requirements (see attached Table).

8. BACKGROUND:

Azinphos-methyl is a non-systemic organophosphate insecticide/acaricide used in a variety of terrestrial food and non-food crops. It can be formulated as a single ingredient or with other active ingredients (usually other structurally related insecticides).

The Registration Standard for AZINPHOS-METHYL was issued in September 1986 and numerous environmental fate data gaps were noted at that time, some of which have been fulfilled by the regsitrant at a later time (refer to "Table A- Status of Data Requirements").

Azinphos-Methyl is a Restricted Use Pesticide (inhalation hazard to humans).

9. DISCUSSION OF INDIVIDUAL STUDIES: See attached DER.

10. COMPLETION OF ONE-LINER: No new data was entered in the One-Liner at this time.

11. CBI APPENDIX: No CBI.

TABLE A. AZINPHOS-METHYL: Status of Environmental Fate Data Requirements

Data Requirement	MRID #	Acceptability	Status of Requirement
161-1 Hydrolysis	00029899	Yes Science Chapter, 6/26/86	Fulfilled[1]
161-2 Photodegradation in Water	40297001	Yes 12/11/87; EFGWB #70971	Fulfilled[1]
161-3 Photodegradation on Soil	40297002	Yes 12/11/87; EFGWB #70971	Fulfilled[1]
161-4 Photodegradation in Air			Reserved[2]
162-1 Aerobic Soil Metabolism	00029900	Yes Science Chapter, 6/26/86	Fulfilled[1]
162-2 Anaerobic Soil Metabolism	00029900	Yes Science Chapter, 6/26/86	Fulfilled[1]
162-1 Anaerobic Aquatic Metabolism	-	Waived 3/1/88; EFGWB #80294	Waived
162-4 Aerobic Aquatic Metabolism			Not Applicable

[1] The registrant has been requested (EFGWB #91-0915) to address the formation/fate/transport of degradates containing solely an organophosphate moiety.

[2] These studies are RESERVED pending final evaluation of the vapor pressure determination study.

TABLE A. AZINPHOS-METHYL: Status of Environmental Fate Data Requirements

Data Requirement	MRID #	Acceptability	Status of Data Requirement
163-1 Mobility in Soil (Soil Column Leaching; Adsorption/Desorption)	00029885 00029887	These studies appear in the Science Chapter as acceptable and to fulfill data requirements. However, under current requirements these studies would not fulfill requirements. Batch-equilibrium adsorption desorption studies with parent azinphos-methyl in an agricultural sand (<1% OM) and with each major degradate (four soils) are still required.	
163-2 Volatility from Soil (Lab.)			Reserved[2]
163-3 Volatility from Soil (Field)			Reserved[2]
164-1 Terrestrial Field Dissipation	00144667 00144669 00144673	A series of terrestrial field dissipation studies (at 4 lb ai/A) were reviewed at the for the Registration Standard and found acceptable to fulfill data requirements. However, <u>under current guidelines these studies would not be acceptable</u> (depth of sampling 12-inches instead of the minimum 36-inches currently required). All the studies were conducted in the late seventies. <u>New studies are required</u>.	
164-2 Aquatic (sediment) Field Dissipation			Not Applicable
164-3 Forestry Dissipation	Waived	3//1/88; EFGWB #80294	Waived
164-4 Dissip. Combination/Tank Mixes			Not currently imposed
164-5 Terrestrial Field Dissipation (Long-term)			Reserved

TABLE A: AZINPHOS-METHYL: Status of Environmental Fate Data Requirements

Data Requirement	MRID #	Acceptability	Status of Data Requirement
Accumulation Studies:			
165-1 In Confined Rotational Crops	41393601 Submitted 2/28/90	Reviewed 12/20/91 and found not acceptable at the time. Acceptability depends on satisfactory additional information. EFGWB #91-0915	
165-2 Rotational Crops (Field)			Reserved
165-3 In Irrigated Crops	Waiver Request 04/05/88	This waiver request had not been seen by EFGWB. However, in the 1986 Registration Standard the Branch indicated that the 165-3 requirement could be waived if the labels of products containing AZINPHOS-METHYL carry a statement prohibiting use of water leaving treated fields for purposes of irrigating other crops. If the waiver request is based on the recommended label statement, then the 165-3 requirement may be waived.	
165-4 In Fish	00112146	Acceptable Science Chapter, 6/26/86	Fulfilled
165-5 In Aquatic Non-Target Organisms		Waived 3/1/88; EFGWB #80294	Waived

TABLE A AZINPHOS-METHYL: Status of Environmental Fate Data Requirements

Data Requirements	MRID #	Acceptability	Status of Data Requirement
Other Studies			
Ground and/or Surface Water Monitoring Studies			Reserved (See accompanying memorandum).
SPRAY DRIFT STUDIES			
201-1 Droplet Size Spectrum		In a review dated 6/19/87, the submitted drift studies (Accession #073605) were considered unacceptable at the time, but it was indicated that the studies could be upgraded by submission of additional data. There are no records in EFGWB files that the additional data has been received.	
202-1 Drift Field Evaluation.....			

91

APPENDIX

AZINPHOS-METHYL- Environmental Fate

I. SUMMARY

Hydrolysis and photodegradation in water are the fastest degradation routes for azinphos-methyl (half-lives less than one week). Although azinphos-methyl is not rapidly photodegraded or biodegraded in soils (half-lives greater than one month) and not considered to be extremely mobile in soils, azinphos-methyl residues could potentially enter surface water(s) with eroded soil particulates rather than by dissolved run-off, especially if very heavy rainfall events occur immediately after application.

II. DETAILED INFORMATION

a. Hydrolytic stability:
The hydrolysis half-lives of azinphos-methyl at pH 4, 7, and 9 are 39, 23, and 2.2 hours, respectively; hydrolytic stability decreases with increasing pH of the aqueous media. Major degradates are Mercapto-methyl benzazimide and bis-(benzazimide-N-methyl) sulfide.

b. Effect of exposure to sunlight:
In buffered pH 4.4 water azinphos-methyl degraded with a half-life of 76.7 hours; the main degradates were benzazimide (maximum 40% after 87 hours) and anthranilic acid (7.2% at 56 hours). On sandy loam soil the half-life of degradation was 99 days.

c. Biodegradation:
Only data on the aerobic and anaerobic biodegradation of azinphos-methyl on soils are available. Under aerobic conditions, the half-life of azinphos-methyl in sandy loam soils was 44 days; under anaerobic conditions, the half-life was 68 days. The metabolites detected were the "azinphos-methyl oxygen analog", mercaptomethyl benzazimide, benzazimide, hydroxymethyl benzazimide, and bis-methyl benzazimide sulfide. Of these metabolites, the "oxygen analog" reached a maximum of 5% after 190 days under aerobic conditions and 0.6% after 90 days under anaerobic conditions; the benzazimide metabolite reached a maximum of 12% after 120 days under aerobic conditions and 9% under anaerobic conditions (no specific amounts of each metabolites were reported in the study). Most of the residues were found as soil-bound residues. Although the biodegradation of azinphos-methyl is not considered a fast degradation pathway, the results indicate that azinphos-methyl is prone to biodegradation. No data on the aerobic or anaerobic aquatic biodegradation are available in the files.

d. Mobility in Soil:
The results of batch-equilibrium adsorption/desorption studies indicate that parent azinphos-methyl is not expected to be extremely mobile in soils. Aged residues of azinphos-methyl do not appear to be very mobile. However, no data are available for mobility of individual degradates/metabolites of azinphos-methyl.

Parent Azinphos-Methyl

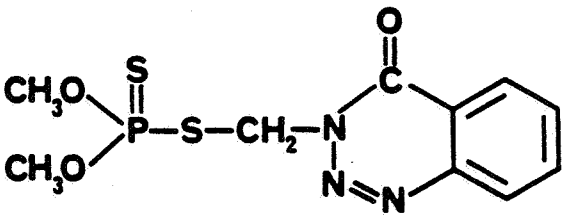
	K_{ads}
Silt loam soil (5% OM; pH 7.9)	16.75
Sandy loam soil (2.8% OM; pH 6.6)	7.60
Silty clay soil (0.5% OM; pH 6.0)	9.85

e. Terrestrial Field Dissipation:
Data indicate that the field dissipation of azinphos-methyl is variable and likely to depend on the type of soil. Half-lives of dissipation vary from 30 days to 181 days. In has been noted in the studies that residues do not move below the 6-inch depth.

f. Bioaccumulation in Fish:
Catfish continuously exposed to azinphos-methyl bioaccumulated total ^{14}C residues at 139x on day 4 of exposure, but averaged 60x during days 7 to 28 of exposure. About 90% of the total residues present on the last day of exposure were released during the 2-week depuration period. However, no data are available on the distribution and nature of the residues in the different parts of the fish. The results indicate that bioaccumulation occurs in the earlier stages of exposure, but it is not known from the available data if fish were exposed to parent azinphos-methyl alone or to any of its degradates.

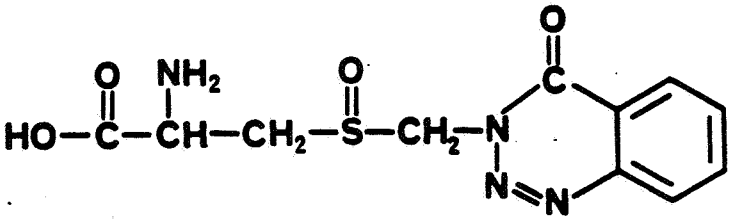
APPENDIX

AZINPHOS-METHYL AND ITS DEGRADATES



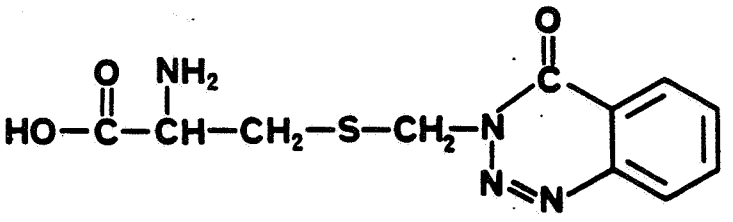
O,O-Dimethyl S-((4-oxo-1,2,3-benzotriazin-4(3H)-yl)methyl) phosphorodithioate

(Azinphos-methyl)



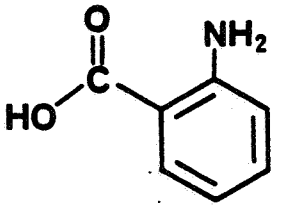
Cysteinylmethylbenzazimide sulfoxide

(Cys-MeBzaz sulfoxide; Cys-MeBaza-SO)



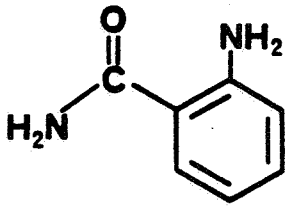
Cysteinylmethylbenazimide

(Cys-MeBzaz)



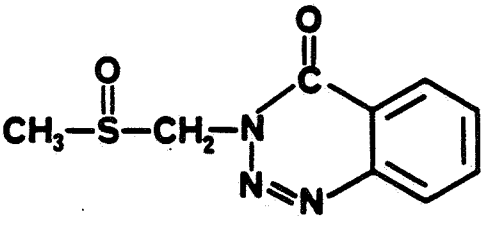
2-Aminobenzoic acid

(Anthranilic acid; Anthra acid)



2-Aminobenzamide

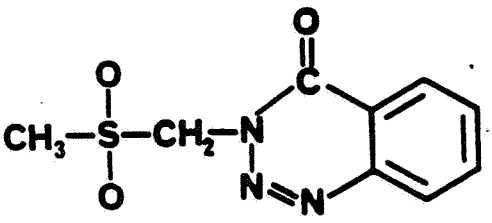
(Anthranilamide)



Methylthiomethylbenzazimide sulfoxide

Methylsulfinylmethylbenzazimide

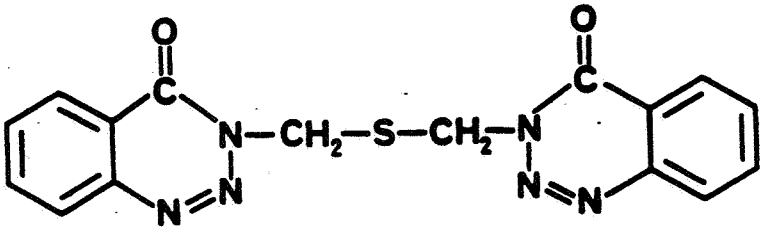
(Me-Thio-MeBzaz sulfoxide; MTMB-SO)



Methylthiomethylbenzazimide sulfone

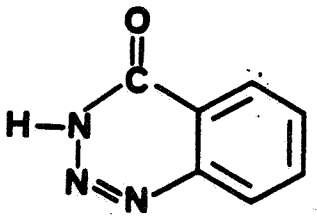
Methylsulfonylmethylbenzazimide

(Me-Thio-MeBzaz sulfone; MTMB-SO_2)



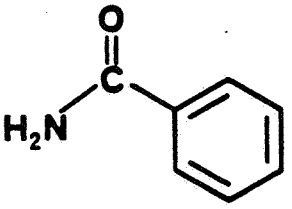
Bis-(methylbenzazimide) sulfide

(Bis-MeBzaz-sulfide)

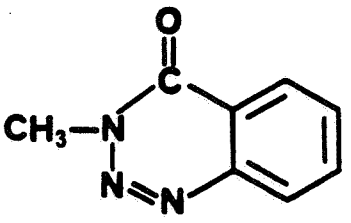


Benzazimide

(Bzaz)



Benzamide



Methylbenzazimide

(MeBzaz)

Azinphos-methyl

Page_____ is not included in this copy.

Pages 21 through 25 are not included.

The material not included contains the following type of information:

____ Identity of product inert ingredients.

____ Identity of product impurities.

____ Description of the product manufacturing process.

____ Description of quality control procedures.

____ Identity of the source of product ingredients.

____ Sales or other commercial/financial information.

____ A draft product label.

____ The product confidential statement of formula.

____ Information about a pending registration action.

X FIFRA registration data.

____ The document is a duplicate of page(s) _____.

____ The document is not responsive to the request.

The information not included is generally considered confidential by product registrants. If you have any questions, please contact the individual who prepared the response to your request.