DATA EVALUATION RECORD

STUDY 1

CHEM 058001 Azinphos-methyl §165-1

FORMULATION--12--EMULSIFIABLE CONCENTRATE (EC)

STUDY ID 41393601
Chopade, H.M., and L.L. Bosnak. 1990. [Phenyl-UL-"C] azinphos-methyl rotational crop study. Mobay Study No. GU05P01. Mobay Report No. 99849. Unpublished study performed and submitted by Mobay Corporation, Stilwell, KS.

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CONCLUSIONS:

Rotational Crops - Confined Accumulation

1. This study is not acceptable at this time for the following reason:

   the length of freezer storage and storage stability data were not provided for the crop or soil residues.

2. ["C]Azinphos-methyl residues accumulated in kale, red beets, and wheat that were planted 30, 135, and 273 days after sandy loam soil was treated with ["C]azinphos-methyl at a nominal rate of 12 lb ai/A. Accumulation was greatest in the 30-day rotational crops, with ["C]residues ranging from 0.18 to 9.84 ppm; accumulation in the 135- and 273-day rotational crops ranged from 0.10 to 2.41 ppm. Six

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degradates were identified in the plant tissues: cysteinylmethylbenzazimide sulfoxide, cysteinylmethylbenzazimide, 2-aminobenzoic acid, 2-aminobenzamide, methylthiomethylbenzazimide sulfoxide, and methylthiomethylbenzazimide sulfone.

3. In order for this study to be accepted and fulfill the accumulation in confined rotational crop data requirement, the registrant must submit data demonstrating that [^{14}C]azinphos-methyl and its degradates are stable in plant tissues and soil when stored frozen. In addition, the registrant must clarify the HPLC detection limits.

METHODOLOGY:

Uniformly phenyl-ring labeled [^{14}C]azinphos-methyl (radiochemical purity >99%, specific activity 22.32 mCi/mMol, Morgan) plus unlabeled azinphos-methyl (purity >99%) were formulated as a 2L emulsifiable concentrate and applied at a nominal field rate of 12 lb ai/A to the surface of sandy loam soil (67% sand, 27% silt, 6% clay, 2.6% organic matter, pH 4.8, CEC 16.0 meq/100 g) with an air-brush. The soil (15 inches deep) was contained in a metal watering trough (approximately 8 x 2 x 2 feet) over a 6-inch layer of gravel in the bottom of the trough. Two hours after application, ten soil cores (0- to 6-inch depth, 1-inch id) were collected; the cores were transferred to ten, 250-mL Erlenmeyer flasks and were mechanically mixed for 2 hours. Four subsamples from each core were radioassayed before the cores were pooled and the soil moisture was determined.

At 30, 135, and 273 days posttreatment, the treated soil was tilled to a depth of 6 inches and planted to red beets, kale, and wheat. In the 30-day rotation, mature kale and immature wheat were harvested at 70 days posttreatment, and mature wheat and red beets were harvested at 135 days posttreatment. In the 135-day rotation, mature kale and immature wheat were harvested at 181 days posttreatment, and mature wheat and red beets were harvested at 223 days posttreatment. In the 273-day rotation, mature kale and immature wheat were harvested at 322 days posttreatment, and mature wheat and red beets were harvested at 360 days posttreatment. After collection, tissue samples were weighed, cut into small pieces, pulverized after freezing with liquid nitrogen, and stored at -10 C (length of storage unspecified). Soil cores were sampled as previously described at 30, 70, 135, 181, 223, 273, 322, and 360 days posttreatment.

Plant tissue was extracted three times with acetonitrile:concentrated HCl (200:0.2, v:v) by grinding in a tissue grinder for 2 minutes and filtering the extract through a 0.45-um filter. The three extracts were pooled. Aliquots were analyzed for total extracted radioactivity by LSC; the remainder was concentrated under vacuum at 25 C and diluted with acetonitrile:methanol (2:1, v:v). Aliquots of the diluted solution were analyzed by LSC. The extracted tissue solids from the 30- and 135-day rotations were refluxed with 2 N NaOH for 3 hours; extracted solids from the 273-day rotation were refluxed

with 2 N HCl for 3 hours. The extracts were filtered through a 0.45-um filter, then neutralized with either HCl or NaOH. The neutralized reflux solutions were centrifuged, the supernatants were decanted, and aliquots were analyzed by LSC. The remaining supernatants were rotary evaporated to dryness as an azeotropic mixture with acetonitrile at 25 C. The residues were dissolved in methanol "leaving salts behind" and were analyzed by LSC and HPLC as described below.

Portions of each soil core were analyzed by LSC following combustion before the cores were pooled. Subsamples (50 g) of the pooled cores were extracted three times with acetonitrile:concentrated HCl (150:0.1, v:v) by grinding in a tissue grinder for 2 minutes and filtering the extract through a 0.45-um filter. The three extracts were pooled. Aliquots were analyzed for total extracted radioactivity by LSC; the remainder was concentrated by rotary evaporation under vacuum at 25 C, diluted with acetonitrile, and mixed. Aliquots of the diluted solution were analyzed by LSC. The acetonitrile solution was again concentrated by rotary evaporation under vacuum to 10 mL and analyzed by HPLC as described below. The extracted soil solids were air-dried for 24 hours, and four subsamples were analyzed by LSC following combustion. A subsample (25 g) of the extracted-soil solids was Soxhlet-extracted for 1.5 hours with methanol:chloroform (1:1, v:v); the extract was cooled, the volume was determined, and aliquots were analyzed by LSC. The Soxhlet-extracted soil solids were air-dried at room temperature and refluxed with methanol:HCl (150:1, v:v) for 1.5 hours. The reflux extract was cooled and filtered (0.45 um); the volume was determined and aliquots were analyzed by LSC. The methanol:HCl extract was vacuum evaporated at 25 C to dryness; the residue was dissolved in methanol, and aliquots were analyzed by LSC. The extracted soil was air-dried and analyzed by LSC following combustion.

Analytical procedures: To prepare samples for HPLC analysis, aliquots of the organic extracts were spiked with analytical standards and dried under a stream of nitrogen. The residue was dissolved in 0.1 mL of methanol or acetonitrile and 1.7-2 mL of the appropriate starting mobile phase. Two HPLC systems were used. System A used an ODS-3 column with a mobile phase of 0.005 M pentyltriethylammonium phosphate:methanol, starting with 100% pentyltriethylammonium phosphate and ending with 100% methanol. System B used a PRP-1 column with a mobile phase of 0.1% acetic acid:acetonitrile starting with 100% acetic acid followed by a linear gradient ending with 100% acetonitrile. Both systems used UV (254 nm) and IN/US radioactivity detection. The identities of compounds isolated from the soil were also confirmed by chemical ionization GC/MS.

DATA SUMMARY:

[^{14}C]Azinphos-methyl residues accumulated (0.10 to 9.84 ppm) in kale, red beets, and wheat that were planted 30, 135, and 273 days after sandy loam soil was treated with phenyl-ring labeled [^{14}C]azinphos-methyl plus unlabeled azinphos-methyl (radiochemical purities >99%, formulated as a 2 lb ai/gallon EC) at a nominal field rate of 12 lb ai/A. Accumulation was greatest in the 30-day rotational crops, with [^{14}C]residues ranging from 0.18-9.84 ppm; accumulation in the 135- and 273-day rotational crops ranged from 0.10 to 2.41 ppm (Table V). Mature wheat straw contained the greatest concentration of residues with 9.84, 1.68, and 2.41 ppm for the 30-, 135-, and 273-day rotations, respectively (Table VIII). Six degradates were identified in the plant tissues:

cysteinylmethylbenzazimide sulfoxide (Cys-MeBzaz-SO);

cysteinylmethylbenzazimide (Cys-MeBzaz);

2-aminobenzoic acid (anthranilic acid);

2-aminobenzamide (anthranilamide);

methylthiomethylbenzazimide sulfoxide (MTMB-SO); and,

methylthiomethylbenzazimide sulfone (MTMB-SO_2).

In the 30-day rotation, all crops contained between 0.18 and 9.84 ppm radioactivity (Table V). Immature wheat contained a total of 1.07 ppm extracted radioactivity, which consisted of 0.37 ppm Cys-MeBzaz-SO, 0.26 ppm MTMB-SO, and 0.43 ppm MTMB-SO_2 (Table IX). Mature kale contained a total of 0.55 ppm extractable radioactivity, which consisted of 0.17 ppm Cys-MeBzaz-SO, 0.10 ppm MTMB-SO, and 0.28 ppm MTMB-SO_2. Mature wheat heads contained a total of 1.47 ppm extracted radioactivity, which consisted of 0.70 ppm Cys-MeBzaz-SO, 0.59 ppm anthranilamide, 0.02 ppm MTMB-SO, 0.14 ppm MTMB-SO_2, and 0.02 ppm of unidentified radioactivity. Mature wheat straw contained a total of 8.76 ppm extracted radioactivity, which consisted of 3.35 ppm Cys-MeBzaz-SO, 2.56 ppm anthra acid, 0.49 ppm anthranilamide, 0.10 ppm MTMB-SO, and 2.16 ppm MTMB-SO_2. Mature red beet tops contained a total of 0.68 ppm extracted radioactivity, which consisted of 0.17 ppm Cys-MeBzaz-SO, 0.07 ppm Cys-MeBzaz, 0.02 ppm anthra acid, 0.02 ppm MTMB-SO, and 0.39 ppm MTMB-SO_2. Red beet roots contained a total of 0.11 ppm extracted radioactivity, which consisted of 0.03 ppm MTMB-SO, 0.04 ppm MTMB-SO_2, and 0.03 ppm of unidentified radioactivity.

In the 135-day rotation, all crops contained between 0.10 and 1.68 ppm radioactivity (Table V). Immature wheat contained a total of 0.31 ppm extracted radioactivity, which consisted of 0.24 ppm Cys-MeBzaz-SO, 0.03 ppm anthra acid, and 0.04 ppm of unidentified radioactivity (Table X). Mature kale contained a total of 0.22 ppm

extracted radioactivity, which consisted of 0.10 ppm MTMB-SO, 0.11 ppm MTMB-SO_2, and 0.01 ppm of unidentified radioactivity. Mature wheat heads contained a total of 0.17 ppm extracted radioactivity, which consisted of 0.07 ppm Cys-MeBzaz-SO, and 0.10 ppm of unidentified radioactivity. Mature wheat straw contained a total of 1.11 ppm extracted radioactivity, which consisted of 0.49 ppm Cys-MeBzaz-SO, 0.10 ppm Cys-MeBzaz, 0.05 ppm anthra acid, 0.12 ppm MTMB-SO, 0.03 ppm MTMB-SO_2, and 0.30 ppm of unidentified radioactivity. Mature red beet tops contained a total of 0.33 ppm extracted radioactivity, which consisted of 0.09 ppm Cys-MeBzaz-SO, 0.14 ppm anthra acid, and 0.09 ppm MTMB-SO_2. Red beet roots contained a total of 0.08 ppm extracted radioactivity, which consisted of 0.04 ppm MTMB-SO_2, and 0.04 ppm of unidentified radioactivity.

In the 322-day rotation, all crops contained between 0.25 and 2.41 ppm radioactivity (Table V). Immature wheat contained a total of 0.50 ppm extracted radioactivity, which consisted of 0.19 ppm Cys-MeBzaz-SO, 0.10 ppm MTMB-SO, and 0.21 ppm MTMB-SO_2 (Table XI). Mature kale contained a total of 0.25 ppm extractable radioactivity, which consisted of 0.06 ppm Cys-MeBzaz-SO, 0.04 ppm MTMB-SO, 0.11 ppm MTMB-SO_2, and 0.07 ppm of unidentified radioactivity. Mature wheat heads contained a total of 0.25 ppm extracted radioactivity, which consisted of 0.12 ppm Cys-MeBzaz-SO, 0.03 ppm Cys-MeBzaz, 0.03 ppm MTMB-SO, and 0.09 ppm of unidentified radioactivity. Mature wheat straw contained a total of 0.58 ppm extracted radioactivity, which consisted of 0.10 ppm Cys-MeBzaz-SO, 0.13 ppm Cys-MeBzaz, 0.19 ppm MTMB-SO, 0.07 ppm MTMB-SO_2, and 0.07 ppm of unidentified radioactivity. Mature red beet tops contained a total of 0.91 ppm extracted radioactivity, which consisted of 0.21 ppm Cys-MeBzaz-SO, 0.23 ppm MTMB-SO, 0.36 ppm MTMB-SO_2, and 0.10 ppm of unidentified radioactivity. Red beet roots contained a total of 0.20 ppm extracted radioactivity, which consisted of 0.01 ppm Cys-MeBzaz-SO, 0.11 ppm MTMB-SO, 0.03 ppm MTMB-SO_2, and 0.05 ppm of unidentified radioactivity.

The soil contained 14.17 ppm azinphos-methyl residues immediately posttreatment, 6.15 ppm at 30 days (first planting), 4.61 ppm at 135 days (second planting), 3.74 ppm at 273 days (third planting) and 3.20 ppm when the study was terminated at 360 days (Table IV). The parent compound was not detected in soil samples taken after 135 days posttreatment. Four degradates, MTMB-SO, MTMB-SO2, anthranilic acid, and

bis-(methylbenzazimide) sulfide (Bis-MeBzaz-sulfide),

were extracted from the soil at all sampling intervals after day 0 at 0.09-0.80 ppm. Small amounts (<0.03-0.13 ppm) of

benzazimide (Bzaz),

benzamide, and

methylbenzazimide (MeBzaz)

were extracted from soil at some sampling intervals. Unidentified radioactivity ranged from 0.04-0.56 ppm (Table VII).

Air temperatures surrounding the soil trough in both the greenhouse and outdoors ranged from 30 to 111 F.

COMMENTS:

1. Freezer storage stability data were not provided for azinphos-methyl and its residues in plant tissues and soil. The length of storage time was also not provided.

2. HPLC detection limits were not reported. In Tables IX-XI, data for some sampling intervals were cited as <0.01 ppm for Cys-MeBzaz-SO, Cys-MeBzaz, and MTMB-SO.

3. The theoretical rate of application of 12 lb ai/A should have resulted in a 6 ppm azinphos-methyl concentration in the top 6 inches of soil immediately following application. The measured level at day 0 (approximately 2 hours posttreatment) was 14.17 ppm. The study authors stated that this measured level was incorrect and was probably caused by contamination from the open-sided corer used to take the samples.

4. Ten soil cores were taken at plantings (30, 135, and 273 days posttreatment) and at the harvest of mature wheat and beets (223 and 360 days posttreatment). Six soil cores were taken at sampling of immature wheat and mature kale (70, 181, and 322 days posttreatment).

5. Crops in the trough were maintained outside during September 1987; the trough was moved into the greenhouse in October, and remained in the greenhouse until April 1988. In April, the container was moved outdoors and remained outdoors until the termination of the study in July 1988.

6. For this study, an emulsifiable concentrate was formulated from active ingredients. Uniformly phenyl-ring labeled [^{14}C]azinphos-methyl (radiochemical purity >99%, specific activity 22.32 mCi/mMol, Morgan) plus unlabeled azinphos-methyl (purity >99%) were dissolved in benzene. The benzene was evaporated under a stream of nitrogen, a blank formulation (87RO234I) was added (9.1 mL), and the azinphos-methyl was dissolved by shaking; the solution was made to 100 mL with deionized water and shaken. An aliquot was taken for analysis by HPLC.

7. The soil in the trough had been planted to rye grass which was removed a few days prior to the azinphos-methyl application.

8. The detection limit for the combustion of plant tissue or soil was 0.01 ppm.

9. Varying amounts of plant tissue were extracted: 17-40 g immature wheat; 50 g of kale, beet roots and beet tops; 20 g mature wheat straw (presoaked with 20 mL of water); and 25 g mature wheat heads (presoaked with 25 mL of water).

10. There were apparent typographical errors in Tables VII and VIII. In Table VII, the total for "others" at day 135 is 0.10 ppm; in Table VIII, the total concentration for red beet roots at 223 and 360 days are 0.10 and 0.25 ppm, respectively.

Azinphos-methyl

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Pages 8 through 20 are not included.

The material not included contains the following type of information:

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____ Identity of product impurities.

____ Description of the product manufacturing process.

____ Description of quality control procedures.

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____ Sales or other commercial/financial information.

____ A draft product label.

____ The product confidential statement of formula.

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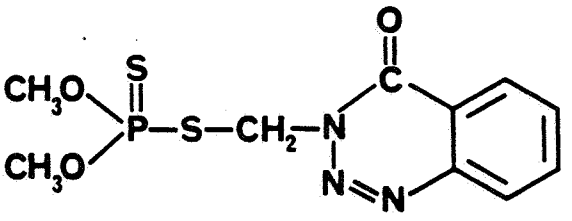
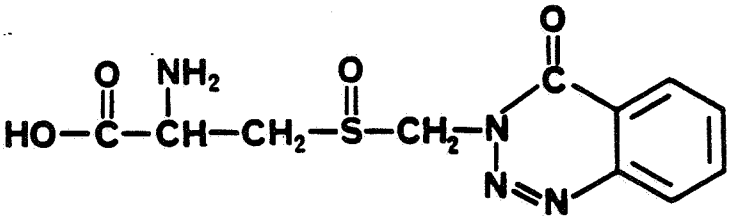
APPENDIX

AZINPHOS-METHYL AND ITS DEGRADATES



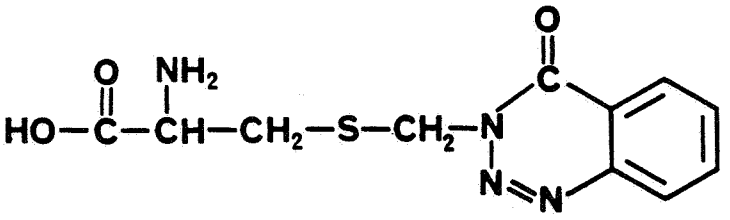
O,O-Dimethyl S-((4-oxo-1,2,3-benzotriazin-4(3H)-yl)methyl) phosphorodithioate

(Azinphos-methyl)



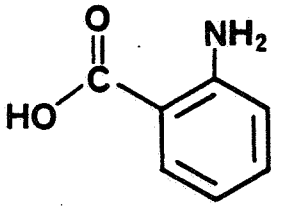
Cysteinylmethylbenzazimide sulfoxide

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



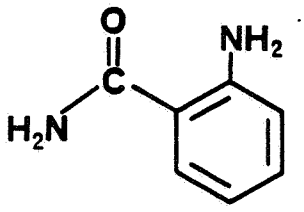
Cysteinylmethylbenazimide

(Cys-MeBzaz)



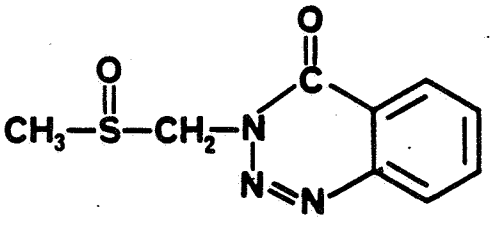
2-Aminobenzoic acid

(Anthranilic acid; Anthra acid)



2-Aminobenzamide

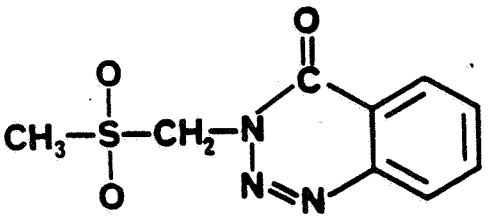
(Anthranilamide)



Methylthiomethylbenzazimide sulfoxide

Methylsulfinylmethylbenzazimide

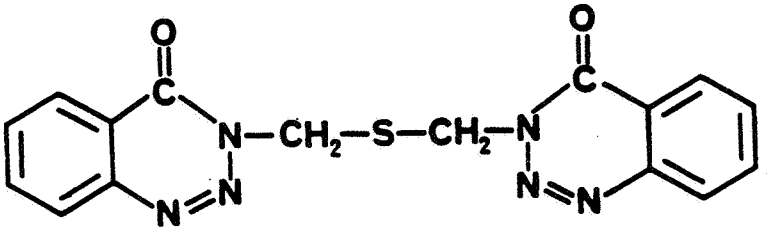
(Me-Thio-MeBzaz sulfoxide; MTMB-SO)



Methylthiomethylbenzazimide sulfone

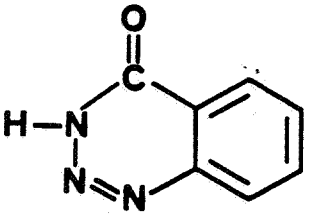
Methylsulfonylmethylbenzazimide

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



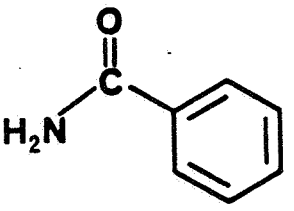
Bis-(methylbenzazimide) sulfide

(Bis-MeBzaz-sulfide)

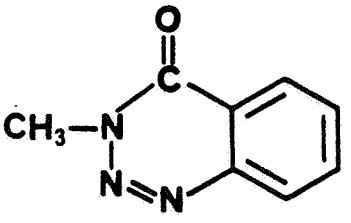


Benzazimide

(Bzaz)



Benzamide



Methylbenzazimide

(MeBzaz)