DYNAMAC
CORPORATION

AMITRAZ ADDENDUM

Task 1: Review and Evaluation of Individual Studies

Task 2: Environmental Fate Assessment

January 27, 1989

Final Report

Contract No. 68-02-4250

Submitted to:
Environmental Protection Agency
Arlington, VA 22202

Submitted by:
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INTRODUCTION

Amitraz is an insecticide/acaricide registered for control of the pear psylla and mites on pears as a foliar spray using air or ground equipment. The most commonly used equipment is the air blast sprayer. All formulations are single active ingredient and consist of a 1.5 lb/gal EC and a 50% WP. The 1.5 lb/gal EC may be applied to pears at a rate of 0.75-0.94 lb ai/A, as a 0.188-0.375 lb/100 gal concentration, or as a 3-6 oz/100 gal concentration. The 50% WP may be applied to pears at a rate of 0.75-1.5 lb ai/A or as a 3-6 oz/100 gal concentration. The label states that amitraz may not be applied to water because it is toxic to fish. Mixers and applicators must wear protective clothing. Applicators may, alternatively, use a tractor cab or airplane cockpit having a properly filtered air supply.

AMITRAZ ADDENDUM

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DATA EVALUATION RECORD

STUDY 1

CHEM 106201 Amitraz 161-1

FORMULATION--00--ACTIVE INGREDIENT

STUDY ID 40780512
Campbell, J.K. 1988. W89 Amitraz: The hydrolysis of amitraz in aqueous solution at 25 C under acid neutral and alkaline conditions. Laboratory Project ID ENVIR/88/4. Unpublished study prepared by Schering Agrochemicals Limited, Walden, Essex, England, and submitted by Nor-Am Chemical Co., Wilmington, DE.

DIRECT REVIEW TIME = 12

REVIEWED BY: W. Hurtt TITLE: Staff Scientist

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CONCLUSIONS:

Degradation - Hydrolysis

1. This study is acceptable and fulfills EPA Data Requirements for Registering Pesticides by providing information on the hydrolysis of amitraz in sterile aqueous solutions buffered to pH 5, 7, and 9.

2. ^{14}C-amitraz degraded with a half-lives of 2.1 hours at pH 5, 22.1 hours at pH 7, and 25.5 hours at pH 9.

3. Degradates were BTS 27919, BTS 24868, and BTS 27271. See Appendix for chemical structures and names.

SUMMARY OF DATA BY REVIEWER:

Ring-labeled [^{14}C]amitraz (radiochemical purity 95%), at 0.04 or 0.05 ppm, degraded in the dark at 25 C in sterile buffers containing 1% acetone with registrant-calculated half-lives of 2.1 hours in the pH 5 solution, 22.1 hours in the pH 7 solution, and 25.5 hours in the pH 9 solution. At the termination of the hydrolysis experiments, amitraz comprised ca 8% of the pH 5 solution (7.33 hours), ca.20% of the pH 7 solution (49.1 hours), and ca.13% of the pH 9 solution (74.4 hours). Similarly, the major degradate . . .

2,4-dimethylformanilide (BTS 27919)

comprised ca.62% of the applied radioactivity in the pH 5 solution (7.33 hours), ca.38% of the radioactivity in the pH 7 solution (49.1 hours), and ca.85% of the radioactivity in the pH 9 solution (74.4 hours). A second degradate . . .

2,4-dimethylaniline (BTS 24868)

comprised ca.17, 17, and 1% of the applied radioactivity in the pH 5, 7, and 9 solutions, respectively. A third degradate . . .

N-2,4-dimethylphenyl-N'-methylformamidine (BTS 27271)

comprised ca.11, 23, and 1% of the applied radioactivity in the pH 5, 7, and 9 solutions, respectively. The material balance (recovery in the final extract) varied from 82.6 to 109.4% in the pH 5 solution, 76.6 to 101.8% in the pH 7 solution, and 78.0 to 123.4% in the pH 9 solution.

DISCUSSION:

1. The 0.05-ppm concentration of amitraz employed in this study was lower than that suggested by the guidelines, but the study author had few options since the reported solubility of amitraz in water is only 0.1 mg/L.

2. Volatilization was only indirectly addressed; however, there was no evidence to suggest that it affected the results.

MATERIALS AND METHODS

MATERIALS AND METHODS:

Ring-labeled [^{14}C]amitraz (radiochemical purity 95%, specific activity 136 mCi/g, Amersham International, Ltd.) dissolved in acetone was added to sterile (autoclaved) glass-distilled water buffered at pH 5 (potassium hydrogen phthalate plus potassium chloride), pH 7 (disodium hydrogen phosphate plus sodium dihydrogen phosphate), or pH 9 (sodium tetraborate plus sodium chloride) to make a final concentration of 0.051 ppm in the pH 5 and 7 solutions and 0.041 ppm in the pH 9 solution. The final acetone concentration in the solutions was 1%. The three solutions were incubated in the dark at 25C in 500-mL flasks covered with aluminum foil and sampled over the following intervals: pH 5, 0-7.3 hours; pH 7, 0-49.1 hours; and pH 9, 0-74.4 hours.

After sampling at the designated intervals, the samples were extracted with methylene chloride. The methylene chloride extracts were dried at -70C by filtering through glass fiber paper (which removed ice crystals) and concentrated at 65C in a column-fitted flask with anthracene. Total radioactivity in the samples was determined by LSC analysis, and amitraz and its degradates were isolated and identified by HPLC. Recovery was determined at the various extraction stages by LSC.

DATA EVALUATION RECORD

STUDY 2

CHEM 106201 Amitraz 161-2

FORMULATION--00--ACTIVE INGREDIENT

STUDY ID 40780513
Brehm, M. 1988. W101 Amitraz: The photolysis of amitraz (Schering Code No. ZK 49 974) in aqueous solution. Laboratory Project ID# APC 06/88:87/114. Unpublished study prepared by Schering AG, Berlin, Germany, and submitted by Nor-Am Chemical Co., Wilmington, DE.

DIRECT REVIEW TIME = 12

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CONCLUSIONS:

Degradation - Photodegradation in Water

This study is scientifically sound and provides supplemental information on the aqueous photolysis of amitraz. The study does not fulfill EPA data requirements for registering pesticides because the mercury arc light source was not comparable to sunlight, the intensity values for sunlight and the arc lamp were not based on actual measurements, and the absorption spectra of amitraz in the test solutions were not provided. Amitraz photodegraded in a buffered, aqueous solution (pH 7, 28 C) with a $t_{1/2}$ = 11.8 hours; the degradates were BTS 27919 (28.4% of applied) and BTS 27271 (13.7%).

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SUMMARY OF DATA BY REVIEWER:

Ring-labeled [^{14}C]amitraz (radiochemical purity >98%), at 0.04 ppm, in pH 7 buffer containing 1% acetonitrile degraded with a registrant-calculated half-life of 11.8 hours at 28C when continuously irradiated with a mercury arc lamp. The observed half-life was ca.7 hours. The calculated intensity of the light within the sample containers was 3.1 mW/cm^2 between 290 and 380 nm compared to 3.8 mW/cm^2 for the theoretical solar radiation value for sunlight at 40 deg northern latitude. The dark controls degraded with a calculated half-life of 15.9 hours and an observed half-life of 7-25 hours. When the study author adjusted the data for the dark control, the computed half-life was 46.5 hours. The half-lives in sunlight days for spring, summer, and fall at northern latitudes of 20 deg, 40 deg, and 60 deg (as determined by a solar intensity simulation program) ranged from 3.27 days (summer, 20 deg) to 26.4 days (fall, 60 deg). At the termination of the photolysis experiment (30.44 hours), amitraz comprised ¼14% of the applied radioactivity and two major degradates, . . .

2,4-dimethylformanilide (BTS 27919) and

N-2,4-dimethylphenyl-N'-methylformamidine (BTS 27271)

comprised 28.4 and 13.7%, respectively, of the applied radioactivity. The comparable terminal percentage values for the dark controls at 29.85 hours were 25.1% amitraz, 44.5% BTS 27919, and 24.1% BTS 27271. The material balance ranged from 91.9 to 105.1% of the applied in the dark controls and 96.6 to 103.4% in the irradiated solutions.

DISCUSSION:

1. The light source was not comparable to sunlight because it was discontinuous and had no emission beyond ca.450 nm. The information pertaining to the lamp was based upon data supplied by the manufacturer of the lamp and not on actual measurements. Similarly, the intensity of the light in the area of or within the sample containers was calculated rather than measured. In determining the half-life of amitraz in "sunlight days", a solar intensity simulation program was used rather than actual measurements of sunlight intensity.

2. The absorption spectra of amitraz in the test solution was not provided. The spectra provided was for a solution containing 55% acetonitrile rather than the 1% that was used in the actual irradiation experiments.

3. Based on preliminary solubility experiments, the study author noted that the solubility of amitraz reported in the literature was too high and reproducible results could not be obtained using the reported solubility. The study author felt that the 0.04 ppm concentration chosen was the best compromise between solubility and radioactivity.

4. The study author also noted that amitraz exhibited a tendency to adhere

to glassware. This effect was partially offset by rinsing the glassware with unlabeled amitraz prior to use.

5. Volatility was not measured. However, the percent recovery values and sum of activities in the radioactive peaks from the HPLC analyses support the study author's statement that there was no evidence for the formation of volatile products.

6. EPA guidelines recommend that photolysis studies be conducted at the pH which minimizes hydrolytic breakdown; for amitraz this value was pH 9 and the associated registrant-calculated half-life was 25.5 hours. However, since the registrant-calculated half-life at pH 7 was 22.1 hours which differed relatively little from 25.5 hours, it is unlikely that the results of the present photolysis study would have been significantly different if conducted at pH 9 rather than pH 7.

7. The method detection limit was not reported.

MATERIALS AND METHODS

MATERIALS AND METHODS:

Ring-labeled [^{14}C]amitraz (radiochemical purity >98%, specific activity 40 mCi/mmol; Amersham International) was added at 0.04 ppm to aqueous (double distilled water) buffered solution adjusted to pH 7 (0.02 M phosphate buffer) containing 1% acetonitrile. Aliquots of the solution were continuously irradiated for 30.44 hours in quartz cuvettes in a revolving photoreactor (Neo Tech-Engineering, Cambridge, England) equipped with a mercury arc lamp (TQ 150, wattage not specified). Computed intensities within the cuvettes were 0.6 mW/cm^2 at 290-320 nm, 0.7 mW/cm^2 at 290-350 nm, 3.1 mW/cm^2 at 290-380 nm compared to intensities of 0.3 mW/cm^2 at 290-320 nm, 1.9 mW/cm^2 at 290-350 nm, and 3.8 mW/cm^2 at 290-380 nm for computer-generated solar radiation values for summer sunlight at 40° northern latitude (cloudless sky).

The lamp was contained within a solarized borosilicate glass filter tube that filtered out wavelengths <290 nm. Light intensity values within the cuvettes were obtained by calculations using the intensity of the light source, the transmission characteristics of the filter tube, and actinometric measurements (based on the photodegradation of oxalic acid). The glass filter tube and lamp were cooled by a fan that moved an air stream through the tube and over the lamp surface. Additional fans maintained the sample area at 28 ± 2°C. For the dark controls, an equal number of cuvettes were wrapped with aluminum foil and placed near the photoreactor such that they were maintained under the same environmental conditions as the irradiated samples. The dark controls were sampled at intervals from 0.67 to 29.85 hours and the amitraz solutions were sampled from 1.26 to 30.44 hours.

Total radioactivity in aliquots of the test solutions was determined by LSC. Separation of degradates was accomplished by direct analysis (no sample preparation) of 1-mL aliquots with HPLC and radioactive flow monitoring. For identification of the radioactive peaks, an additional irradiation experiment was performed for 24 hours and spiked with a mixture of nonlabeled, potential degradation products. The test solutions were analyzed by HPLC with radioactive flow monitoring and UV detection. Degradates were identified by comparison of their retention times with those of the standards.

DATA EVALUATION RECORD

STUDY 3

CHEM 106201 Amitraz 161-3

FORMULATION--00--ACTIVE INGREDIENT

STUDY ID 00407805
Brehm, M. 1987. W85: The photodegradation of amitraz (Schering Code No. ZK 49974) on soil surfaces. Laboratory Project ID# APC 54/87:87/115. Unpublished study prepared by Schering AG, Berlin, Germany, and submitted by NOR-AM Chemical Co., Wilmington, DE.

DIRECT REVIEW TIME = 10

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CONCLUSIONS:

Degradation - Photodegradation on Soil

This study is acceptable. ^{14}C-amitraz degraded with a half-life of <30 min. The major degradates were BTS 27919 (2,4-dimethylformanilide) at 35.8% and BTS 27271 (N-2,4-dimethylphenyl-N'-methylformanidine) at 10.4%.

SUMMARY OF DATA BY REVIEWER:

Ring-labeled [^{14}C]amitraz (radiochemical purity >98%), at ca.1 kg/ha on a sandy loam soil-TLC plate degraded with an observed half-life of <20 minutes at <30 C when continuously irradiated with a Xenon arc lamp. The calculated intensity of the light within the irradiation chamber was 8.0 mW/cm^2 compared to 3.8 mW/cm^2 for the theoretical solar radiation value for sunlight at 40 deg northern latitude. The dark control

degraded with an observed half-life of >30 minutes. At the termination of the photolysis experiment (30 minutes), amitraz comprised 24.2% of the applied radioactivity and two major degradates, . . .

2,4-dimethylformanilide (BTS 27919) and
N-2,4-dimethylphenyl-N'-methylformamidine (BTS 27271)

comprised 35.8 and 10.4%, respectively, of the applied radioactivity. The comparable terminal percentage values for the dark controls were 45.9% amitraz, 27.0% BTS 27919, and 8.1% BTS 27271. The sum of the radioactivity in the extract of nonirradiated soil samples ca.7 minutes after treatment application and the radioactivity in the soil residues was 97.2% of the applied. The material balances over the 5-, 10-, 20-, and 30-minute irradiation periods for both the irradiated and nonirradiated control samples ranged from a low of 96.4% (irradiated, 5 minutes) to a high of 99.9% (nonirradiated, 30 minutes). The unextractable components of the radioactivity in the soil residues comprising these material balance values were 15.7% (irradiated, 5 minutes) and 20.4% (nonirradiated, 30 minutes). No significant amounts of radioactive volatile products were found in the trapping solutions.

DISCUSSION:

1. The study is acceptable and demonstrated that amitraz degraded with a half-life of <30 min (yielding two major degradates) upon exposure to a Xenon lamp.

MATERIALS AND METHODS

MATERIALS AND METHODS:

A slurry of sieved (<0.2 mm) sandy loam soil (77.7% sand, 13.1% silt, 9.1% clay, pH 5.9, and CEC 5.5 mval) in water/methanol was layered to a depth of ca.0.5 mm on glass TLC plates and dried at 120C; the moisture content after several days of equilibration at room temperature was ca.1.0%. Ring-labeled [^{14}C]amitraz (radiochemical purity >98%, specific activity 136 mCi/mg, Amersham International) dissolved in dioxane was sprayed on segments (3 x 4 cm) of the soil TLC plate at a rate equivalent to ca.1.0 kg/ha. The plates were irradiated in a photoreactor apparatus consisting of a xenon arc lamp (Osram GmbH, Berlin, West Germany; XBF 2500 W/I; wattage not specified) surrounded by a quartz water jacket ((KG 2500 UVQ), an aluminum reflector above the lamp, a solarized Duran 50 glass filter below the lamp, and the TLC plate-containing photoreactor chamber 28 cm below the arc lamp. The chamber was covered with a glass filter plate (WG 295, Shott AG, Mainz, West Germany) which filtered out wavelengths <290 nm, as did the solarized Duran glass filter. The TLC plate was cooled (<30C) on the glass (lower) surface by flowing water and exposed to a flowing air stream on the soil (upper) surface. An external pump pulled the air stream through one trap containing ethylene glycol and two traps containing ethanolamine to trap possible volatile products. Based on preliminary experiments, soil-irradiation times of 5, 10, 20, and 30 minutes were chosen. Each treatment (irradiation period) consisted of three soil segments exposed to light and three dark-control soil segments wrapped in aluminum foil.

Light intensity values within the irradiation chamber were obtained by calculations using: (1) spectral data supplied by the manufacturers of the light source and the filters, and (2) actinometric measurements (based on the photodegradation of oxalic acid). Computed light intensities were 0.2 mW/cm^2 at 290-320 nm, 8.0 mW/cm^2 at 290-380 nm compared to intensities of 0.3 mW/cm^2 at 290-320 nm, and 3.8 mW/cm^2 at 290-320 nm for computer-generated solar radiation values for summer sunlight at 40 deg northern latitude (cloudless sky).

Following irradiation, the soil segments were scraped from the TLC plates into test tubes and extracted with acetonitrile four times followed by centrifugation after each extraction step. The extracts were combined and diluted with acetonitrile to a final volume of 5 mL; the soil residues remaining after the extractions were dried and stored until analysis. Total radioactivity was determined in aliquots of the extracts and HPLC-fractions by LSC, in the soil residues by combustion and LSC, and in aliquots of the trapping solutions by LSC. For separation of the degradates, aliquots of the acetonitrile extracts were diluted with 0.01 M phosphate buffer (adjusted to pH 7 with phosphoric acid) and subjected to HPLC analysis with radioactive flow monitoring and UV detection. For identification of the degradates, retention times were compared between a standard solution containing nonlabeled, potential degradation products and a soil extract (30-minute irradiation time) spiked with the standard solution.

DATA EVALUATION RECORD

STUDY 4

CHEM 106201 Amitraz 162-1 and 162-2

FORMULATION--00--ACTIVE INGREDIENT

STUDY ID 40798003
Somerville, L. 1988. (W5 2nd edn) Degradation of [^{14}C]-radiolabeled amitraz in soil under aerobic, anaerobic and sterile conditions. Laboratory Project ID ENVIR/88/28. Unpublished study prepared by Schering Agrochemicals Limited, Essex, England, and submitted by Nor-Am Chemical Company, Wilmington, DE.

DIRECT REVIEW TIME = 10

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CONCLUSIONS:

Metabolism - Aerobic Soil

The study is acceptable. ^{14}C-amitraz degraded with a half-life of <1 day in silt loam and sandy loam soils. Degradates identified were BTS 27919 (35.4%), BTS 24868 (13.58%), BTS 27271 (12.9%), and $^{14}CO_2$ (24.8-34.5%).

Metabolism - Anaerobic Soil

This portion of the study is scientifically sound and provides supplemental information on the anaerobic soil metabolism of amitraz. The study does not fulfill EPA data requirements for registering pesticides because there was an insufficient amount of parent amitraz remaining when anaerobic conditions were established to assess the degradation of amitraz in soil. In addition, this portion of the study would not fulfill EPA Data Requirements for Registering Pesticides because the

soils were incubated aerobically for 30 days instead of one half-life prior to establishing anaerobic conditions. However, amitraz degraded anaerobically (50% less CO_2 evolved thean from the aerobic study) to yield the degradates BTS 27919 (12.9% of applied), BTS 24868 (5.5%), and BTS 27271 (1.3%) during the 60 day incubation at 25 C.

SUMMARY OF DATA BY REVIEWER:

Metabolism - Aerobic Soil

[^{14}C]Amitraz (radiochemical purity 96%), at 6 ug/g, degraded with a half-life of <1 day in nonsterile silt loam and sandy loam soils incubated at 25 C and 50% moisture capacity. At 1 day posttreatment, <6.95% of the applied was parent compound. Nonvolatile degradates identified were

2,4-dimethylformanilide (BTS 27919; maximum concentration up to 35.41% of the applied at 1 day posttreatment),

2,4-dimethylaniline (BTS 24868; maximum concentration up to 13.58% of the applied at 3 hours posttreatment), and

N-2,4-dimethylphenyl-N'-methylformamidine (BTS 27271; maximum concentration up to 12.90% of the applied at 3 hours posttreatment).

At 364 days posttreatment, $^{14}CO_2$ totaled 24.8-34.5% of the applied and unextractable [^{14}C]residues were 52.9-64.5% of the applied in the two soils. Material balances ranged from 89.1 to 107.9% of the applied.

In sterilized silt loam and sandy loam soils incubated under similar conditions, amitraz degraded with a half-life of <1 day. At 1 day posttreatment, <1.79% of the applied was parent compound. Nonvolatile degradates were identical to those in the nonsterile soils. No $^{14}CO_2$ evolved from the sterile soils during the 30-day study.

Metabolism - Anaerobic Soil

[^{14}C]Amitraz (radiochemical purity 96%) ranged from 0.01 to 0.06 ug/g (0.26 to 1.01% of the applied) during 60 days of incubation under anaerobic conditions (flooded plus nitrogen atmosphere) in silt loam and sandy loam soils at 25 C following 30 days of incubation under aerobic conditions for 30 days at 50% moisture capacity. Three degradates were identified:

2,4-dimethylformanilide (BTS 27919)

at a maximum concentration of 12.93% of the applied following 30 days of anaerobic incubation;

2,4-dimethylaniline (BTS 24868)

at a maximum concentration of 5.53% following 60 days of anaerobic incubation; and

at a maximum concentration of 1.28% following 60 days of anaerobic incubation. Unextractable [^{14}C]residues comprised 72.8-77.5% of the applied and $^{14}CO_2$ totaled 7.1-12.9% of the applied following 60 days of anaerobic incubation. Material balances ranged from 80.0 to 97.9% of the applied during the study.

DISCUSSION:

General

1. The soil moisture content during aerobic incubation was 50% moisture capacity rather than 75% of 0.33 bar.

Metabolism - Aerobic Soil

This portion of the study fulfills data requirements by providing information on the aerobic metabolism of amitraz in silt loam and sandy loam soils.

Metabolism - Anaerobic Soil

1. Parent amitraz was aged for longer than one half-life prior to the establishment of anaerobic conditions, so that there was an insufficient amount of parent material remaining to assess the anaerobic degradation of amitraz in soil. In the silt loam soil, only 0.31% of the applied was amitraz when anaerobic conditions were established. In the sandy loam soil, only 0.79% of the applied was amitraz and/or its degradate, BTS 24686, when anaerobic conditions were established.

MATERIALS AND METHODS

STUDY AUTHOR(S)'S RESULTS AND/OR CONCLUSIONS

PERTINENT DATA TABLES AND FIGURES

MATERIALS AND METHODS:

Metabolism - Aerobic Soil

[^{14}C]Amitraz (radiochemical purity 96%, specific activity 7.44 μCi/mg, The Boots Company, Ltd.), dissolved in n-heptane, was applied at 6 μg/g to air-dried, sieved (2-mm) sterilized and nonsterilized silt loam and sandy loam soils (Table 2) contained in glass pots. The soils were adjusted to 50% of their moisture holding capacity and maintained at 25 ± 2°C within a continuous air-flow apparatus (flow rate not specified). Carbon dioxide-free air was drawn through a chamber containing the glass pots, and then through 0.1 N H_2SO_4, ethanediol, and ethanolamine trapping solutions connected in series (Figure 1). Glass wool was inserted between the tubes of trapping solutions to prevent back flow and reduce the formation of aerosols. The nonsterile soil and gas traps were sampled in triplicate immediately after treatment (soil only),at 1, 2, 7, 14, 21, 30, and 60 days and at 3, 4, 6, 9, and 12 months posttreatment. The sterile soil and gas traps were sampled in triplicate at 0, 1, 2, 7, 14, 21, and 30 days posttreatment.

At the time of sampling, two of the three samples of each soil type were Soxhlet-extracted with toluene that had been dried over sodium sulfate; the remaining soil sample was stored at -18°C for future use if needed. The extracted soil was air-dried and analyzed for unextractable radioactivity by LSC following combustion. The soil extracts were analyzed by TLC on silica gel plates developed in hexane:triethylamine (85:15), diethyl ether:triethylamine (95:5), and cyclohexane:ethyl acetate:triethylamine (5:3:2). Reference compounds were cochromatographed with the samples and, following development, were visualized under UV light. Radioactive areas were located with a TLC linear scanner and/or autoradiography, and quantified by LSC. Also, aliquots of the extracts were analyzed by reverse-phase HPLC with UV detection; radioactivity in various fractions was determined by LSC.

Aliquots of the liquid trapping solutions were analyzed for total radioactivity by LSC. The ethanolamine trapping solution was acidified with sulfuric acid:distilled water (55:500) and attached to a continuous air flow system. Air was bubbled through the acidified ethanolamine, then through two gas washing bottles containing 2 N sodium hydroxide and one bottle containing ethanolamine for one hour. After aeration, aliquots of the acidified ethanolamine and the gas washing solutions were analyzed by LSC. The 2 N sodium hydroxide solutions were analyzed for volatilized $^{14}CO_2$ by barium chloride precipitation.

Metabolism - Anaerobic Soil

Silt loam soil (described above) and sandy loam soils (68% sand, 17% silt, 15 % clay, pH 5.8, CEC 26.0 meq/100g) were treated with [^{14}C]-amitraz at 6 μg/g and incubated aerobically in glass pots for 30 days at 25 ± 2°C as previously described. Following the 30-day aerobic incubation, anaerobic conditions were established by flooding the soil with water to a depth of 2 cm and purging the glass pots with nitrogen. Soil

and gas traps were sampled immediately before establishing anaerobic conditions (30 days posttreatment), and at 44, 60, and 90 days posttreatment (14, 30, and 60 days after anaerobic conditions were established).

The soil samples and washings from the glass pots were centrifuged. The resulting supernatants were directly analyzed by LSC. The soil samples were extracted with toluene, and the extracts were analyzed by TLC as previously described. Nonextractable radioactivity was analyzed by LSC following combustion.

DATA EVALUATION RECORD

STUDY 5

CHEM 106201 Amitraz 163-1

FORMULATION--00--ACTIVE INGREDIENT

STUDY ID 40780515
Arnold, D.J. and K.L. Barrett. 1988. The adsorption equilibrium of amitraz in sand, sandy loam, clay loam, and clay soils. Laboratory Project ID ENVIR/87/45. Unpublished study prepared by Schering Agrochemicals Limited, Essex, England, and submitted by Nor-Am Chemical Company, Wilmington, DE.

DIRECT REVIEW TIME = 8

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CONCLUSIONS:

Mobility - Leaching and Adsorption/Desorption

This study is unacceptable because the soils were sieved too finely (1mm), rather than at 2mm, which would increase the clay content and favor adsorption. Also, desorption was not studied.

SUMMARY OF DATA BY REVIEWER:

Based on batch equilibrium experiments, [^{14}C]amitraz residues were readily adsorbed by sand, sandy loam, clay loam, and clay soils; mean K_d values (concentration in soil - concentration in solution) were 8 for the sand, 12 for the sandy loam, 30 for the silt loam, and 60 for the clay soil. The soils were equilibrated at 25 C for 4 hours in 1:5 soil:calcium chloride solution slurries that had been treated with 0.016-0.081

ug/mL of [^{14}C]amitraz (radiochemical purity 97.3%).

Based on TLC analysis of soil and solution extracts following the 4-hour equilibration period, amitraz comprised 0.18-8.25% of the applied radioactivity. Three major degradates, . . .

2,4- dimethylformanilide (BTS 27919; up to 28.93% of the applied),

N-2,4-dimethylphenyl-N'-methylformamidine (BTS 27271; up to 19.03% of the applied), and

N-2,4-dimethylphenyl-N'-(2,4-dimethylphenyl)formamidine (BTS 28037; up to 14.13% of the applied), . . .

and two minor degradates, . . .

2,4-dimethylaniline (BTS 24868) and

4-formamido-m-toluic acid (BTS 39098)

(together <7.22% of the applied), were identified. Radioactivity remaining at the origin accounted for <2.01% of the applied. One unidentified degradate was isolated at <3.14% of the applied in soil extracts from the silt loam and sand soils.

DISCUSSION:

1. The soils were sieved too finely (1mm); they should have been sieved at 2mm.

2. Since amitraz rapidly hydrolyzes, there is no adequate way to examine the mobility of only the parent compound. Studies using the batch equilibrium, column leaching, or soil TLC techniques required by the EPA guidelines would all produce data for a mixture of parent and its degradates, rather than parent alone. The guideline distinction between unaged and aged leaching studies is therefore somewhat meaningless for this chemical; all studies could be considered equivalent to aged mobility studies.

   The study authors stated that desorption of amitraz was not examined because of the rapid hydrolysis of amitraz, implying that desorption data would be of little value since the [^{14}C]compounds studied would be degradates rather than parent amitraz. However, since rapid degradation occurs under natural conditions, the desorption data on the degradate mixture would approximate what would be observed in the field. Therefore, in order to understand the potential for amitraz residues to leach, desorption as well as adsorption of the existing amitraz residues should have been addressed; the fact that desorption of amitraz would not address parent alone is of little consequence.

3. Distribution coefficients (concentration in soil – concentration in solution) were calculated instead of Freundlich K values.

4. The soil characterized as a clay (USDA) is a silt loam according to the USDA Soil Textural Classification System and is referred to as such in this review. The textural analysis of the sandy loam soil did not equal 100%, and, as a result, the classification could not be confirmed.

5. The cation exchange capacities (26.1, 24.6, and 33.4) are not typical of U.S. soils.

MATERIALS AND METHODS

MATERIALS AND METHODS:

Sand, sandy loam, silt loam, and clay soils (Table 1) were air-dried, sieved (1 mm), and mixed (1 g soil:5 mL solution) with sterilized 0.01 M calcium chloride solutions that had been treated with ring-labeled [^{14}C]amitraz (radiochemical purity 97.3%, specific activity 153.8 ÌCi/mg, Amersham International) at 0.016-0.024, 0.035-0.038, 0.054-0.055, or 0.071-0.081 Ìg/mL. The calcium chloride solutions had been adjusted to pH 8 before mixing in an attempt to reduce the rate of amitraz hydrolysis. Duplicate soil:solution slurries were shaken for 4 hours at 25C, then centrifuged. Aliquots of the supernatants were analyzed for total radioactivity by LSC.

The soil:solution slurries originally containing ca.0.071 Ìg/mL of [^{14}C]-amitraz were filtered through filter paper. The resulting soil fraction was Soxhlet-extracted with methylene chloride for 18 hours; the solution fraction was partitioned into methylene chloride. [^{14}C]Residues in the soil and solution methylene chloride extracts were separated by TLC on silica gel plates developed in toluene:triethylamine (9:1), cyclohexane:-ethyl acetate:triethylamine (5:3:2), or chloroform:methanol:acetic acid (100:7.5:0.1). Reference compounds were cochromatographed with the sample extracts. After development, radioactive compounds on the plates were located and quantified using a TLC linear scanner, and identified by comparison to the UV light-visualized reference compounds.

DATA EVALUATION RECORD

STUDY 6

CHEM 106201 Amitraz 163-1

FORMULATION--00--ACTIVE INGREDIENT

STUDY ID 40931501
Leake, C.R. 1988a. W103: The "aged" leaching of amitraz in three soil types. Laboratory Project ID ENVIR/88/35. Unpublished study prepared by Schering Agrochemicals Limited, Essex, England, and submitted by Nor-Am Chemical Company, Wilmington, DE.

DIRECT REVIEW TIME = 6

REVIEWED BY: H.L. Manning H. L. Manning
TITLE: Microbiologist
ORG: EFGWB/EFED/OPP

APPROVED BY: Paul J. Mastradone Paul J Mastradone
TITLE: Acting Chief, Section 1
ORG: EFGWB/EFED/OPP

CONCLUSIONS:

Mobility - Leaching and Adsorption/Desorption

This study is acceptable and fulfills EPA Data Requirements for Registering Pesticides by providing information on the mobility (column leaching) of aged (3 days) [^{14}C]amitraz in sand, sandy loam, and clay loam soil. The majority of the ^{14}C-residues (82.7-74.8%) were contained in the upper 10 cm of the columns; smaller amounts (5.2-1.55%) of the applied activity were found in the leachate. However, these residues were polar products and not known degradates. Degradates identified were: BTS 27271, BTS 27919, and BTS 24868.

SUMMARY OF DATA BY REVIEWER:

Aged [^{14}C]amitraz residues were mobile in soil columns (30-cm length, 4.6-cm diameter) of sand, sandy loam, and clay loam soils that were treated with 1.38 lb ai/A (1.55 kg ai/ha, maximum field rate) [^{14}C]-ring-labeled amitraz. Radiochemical purity was 96.5%. The columns were leached with 844 ml of 0.01 M $CaCl_2$ solution (50.8 x cross sectional area of column). While the majority of the [^{14}C]residues (82.7-74.8%) were in the upper 10 cm of the column, the residues were distributed throughout the columns, with 5.2-1.55% of applied being found in the leachate. These residues were polar products and not identifiable with known degradates. Material balance ranged from 94.9 to 87.1% of applied for

all the soil columns. Amitraz degraded with a half-life of <2 days. Amitraz was aged aerobically for 3 days at 25 C and 40% moisture capacity. Degradates identified were . . .

BTS 27271 [N-methyl-N'-(2,4-xylyl)formamidine);

BTS 27919 (form-2',4'-xylidide); and

BTS 24868 (2,4-dimethylaniline).

DISCUSSION:

1. Leachate residues represented 5.2-1.5% of applied, were polar products, and were not any of the known degradates.

2. The moisture content of the aged soils (3 days) was 40% of its holding capacity. While this is less than our guidelines recommend (75% of 0.33 bar), it was apparently sufficient for this short incubation period since the hydrolysis and soil metabolism products were present.

MATERIALS AND METHODS:

Three soils from the United Kingdom were tested in the soil columns: a sand soil (0.8% OM), a sandy loam soil (3.3% OM), and a clay loam (5.6% OM). The classification was according to the USDA. Aliquots of the soils were air-dried, sieved (2 mm), treated with 1.38 lb ai/A (maximum field rate), adjusted to 40% of the soil's moisture holding capacity, and incubated for 3 days at 25 þ 2C. The soils were supplied with CO_2-free moist air and monitored for volatile products (ethanediol and ethanolamine traps).

The leaching columns (two per soil) consisted of seven glass segments (4.6 cm i.d. and 5 cm) held together by rubber seals. The columns were packed with untreated moist soil and overlaid with the treated, aged soil (top segment). The columns were leached with water containing 0.01 M $CaCl_2$ by adding ca.50 mL/day for 17 days. Volatile products were collected in the two trapping solutions cited above. The columns were allowed to drain for 48 hours, were disassembled, and each segment separately extracted. The soils were extracted by dichloromethane followed by acetonitrile:water (4:1), each for 18 hours. Both aged soil samples and column segments were extracted.

DATA EVALUATION RECORD

STUDY 7

CHEM 106201 Amitraz 163-1

FORMULATION—00—ACTIVE INGREDIENT

STUDY ID 40780516
Fortsch, A. 1988a. (W91) Mobility of N-(2,4-dimethylphenyl)-N-formyl-amine (BTS 27 919) in the German standard soils 2.1, 2.2 and 2.3. Laboratory Project ID UPSR 6/88 — PA 49 974.7/13. Unpublished study prepared by Schering AG, Berlin, Federal Republic of Germany, and submitted by Nor-Am Chemical Company, Wilmington, DE.

DIRECT REVIEW TIME = 8

REVIEWED BY: J. Harlin TITLE: Staff Scientist

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SIGNATURE:

CONCLUSIONS:

Mobility - Leaching and Adsorption/Desorption

This study is scientifically sound and provides supplemental information towards the registration of amitraz. This study does not fulfill EPA Data Requirements for Registering Pesticides because the columns were eluted with only ca.8 inches of water (400 ml).However, even using this small amount of water (less than half required of column), ^{14}C residues moved through the column (<3.1%) of applied in leachate for all three soils.

SUMMARY OF DATA BY REVIEWER:

[^{14}C]-2,4-Dimethylformanilide residues were mobile in columns (30-cm length, 50-mm diameter) of sand and loamy sand soils that were treated with 2-methyl-labeled [^{14}C]-2,4-dimethylformanilide (BTS 27919, purity >99%) at 0.82 kg/ha and leached with 200 mm (ca.8 inches) of deionized water; [^{14}C]residues were distributed throughout the columns. Following leaching, 33.0-43.4% of the applied radioactivity remained in the upper 10 cm of the sand (CEC 2.5 mval/100 g) soil column, 29.2-42.2% remained in the upper 10 cm of one loamy sand (CEC 5.4 mval/100 g) soil column, and 68.4-86.2% remained in the upper 10 cm of a second loamy sand soil (CEC 8.0 mval/100 g) soil column. For all three soils, 3.1% of the applied was recovered in the leachate. Approximately 8-36% of the applied radioactivity was methanol-extractable; only 2,4-dimethylformanilide and polar compounds were detected in the extracts. Material balances ranged from 85.9 to 90.4% for all of the soil columns.

DISCUSSION:

1. The columns were eluted with only 20 cm (ca.8 inches) of water, rather than the 50.8 cm (20 inches) of water required by the guidelines.

2. The German Standard Soil 2.3 that was characterized as a sandy loam is a loamy sand according to the USDA Soil Textural Classification System. It is referred to as a loamy sand in this review. In addition, the textural analysis of that soil totaled 100.4%.

3. No quantitative data were provided for TLC analyses of the soil extracts.

MATERIALS AND METHODS

MATERIALS AND METHODS:

One sand and two loamy sand soils (Table 1) were air-dried, sieved (2 mm), and packed to a depth of 30 cm in glass columns (internal diameter 5.0 cm; three columns per soil); column packing was facilitated with a vibrator. The columns of soil were drenched with deionized water and allowed to drain. Then, the soil surfaces were treated with 2-methyl-labeled [^{14}C]2,4-dimethylformanilide (BTS 27919, purity >99%, specific activity 15.1 ìCi/mg, Schering Agrochemicals Ltd.), dissolved in acetone, at ca.0.82 kg/ha (which the study author stated was equivalent to an application rate of 1.61 kg of "totally hydrolyzed" amitraz per hectare). The columns were covered with glass filter plates, wrapped for protection from light, and eluted with a total of ca.200 mm (ca.8 inches) of deionized water for two days.

The leachate was collected after one and two days, and aliquots were analyzed for total radioactivity by LSC. It was stated that TLC analysis of the leachate was not conducted because of the low concentration of radioactive residues.

After leaching, the soil columns were divided into 2-, 5-, or 10-cm segments. Soil from each segment was extracted in methanol and centrifuged. The extracted soil was air-dried, ground to a fine powder, and analyzed for total radioactivity by LSC following combustion. Aliquots of the methanol extracts were concentrated on a rotary evaporator and analyzed for total radioactivity by LSC; aliquots that contained 1000 dpm of extracted material were analyzed by TLC. The TLC analyses were conducted on silica gel plates developed in cyclohexane:ethyl acetate:diethyl amine (5:3:2) and n-hexane:triethyl amine (17:3). Following development, areas of radioactivity were located and quantified using a TLC linear analyzer. The reported detection limits were 0.15% of the applied for LSC analysis of the leachate, 0.09% of the applied for LSC analysis of the soil extracts, and 0.07-0.36% of the applied for LSC analysis of combusted soil.

DATA EVALUATION RECORD

STUDY 8

CHEM 106201 Amitraz 163-1

FORMULATION--00--ACTIVE INGREDIENT

STUDY ID 40780516
Fortsch, A. 1988b. W102 Amitraz: Mobility of N-(2,4-dimethylphenyl)-N-methyl-formamidine (BTS 27 271) in the German standard soils 2.1, 2.2 and 2.3. Laboratory Project ID UPSR 7/88 — PA 49 974.7/13. Unpublished study prepared by Schering AG, Berlin, Federal Republic of Germany, and submitted by Nor-Am Chemical Company, Wilmington, DE.

DIRECT REVIEW TIME = 6

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APPROVED BY: H. Manning
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CONCLUSIONS:

Mobility - Leaching and Adsorption/Desorption

This study is scientifically sound and provides supplemental information towards the registration of amitraz. This study does not fulfill EPA Data Requirements for Registering Pesticides because the columns were eluted with only ca.8 inches of water (400 ml). However, even using this small amount of water (less than half required of column), ^{14}C residues moved through the column (<0.3%) of applied in leachate for all three soils.

SUMMARY OF DATA BY REVIEWER:

[^{14}C]N-2,4-Dimethylphenyl-N'-methylformamidine residues were relatively immobile in columns (30-cm length, 50-mm diameter) of sand and loamy sand soils that were treated with 2-methyl-labeled [^{14}C]N-2,4-dimethylphenyl-N'-methylformamidine (BTS 27271, purity 95%) at 0.82 kg/ha and leached with ca.200 mm (ca.8 inches) of deionized water. Following leaching, 73.6-91.3% of the applied radioactivity remained in the upper 4-5 cm of the soil columns and 0.3% of had been leached from the columns. Approximately 11-22% of the radioactivity applied to the soil was methanol-extractable after 2 days of leaching. N-2,4-Dimethylphenyl-N'-methylformamidine (BTS 27271) and 2,4-dimethylformanilide (BTS 27919) were identified in the extracts in a ratio of ca.9:1 in the sand soil, 19:1 in one loamy sand soil, and 4:5 in a second loamy sand soil. Material balances ranged from 80.6 to 92.1% for all of the soil columns.

DISCUSSION:

1. The columns were eluted with only 20 cm (ca.8 inches) of water, rather than the 50.8 cm (20 inches) of water required by the guidelines.

2. The German Standard Soil 2.3 that was characterized as a sandy loam is a loamy sand according to the USDA Soil Textural Classification System. It is referred to as a loamy sand in this review. In addition, the textural analysis of that soil totaled 100.4%.

3. No quantitative data were provided for TLC analyses of the soil extracts.

MATERIALS AND METHODS

MATERIALS AND METHODS:

One sand and two loamy sand soils (Table 1) were air-dried, sieved (2 mm), and packed to a depth of 30 cm in glass columns (internal diameter 5.0 cm; three columns per soil); column packing was facilitated with a vibrator. The columns of soil were drenched with deionized water and allowed to drain. Then, the soil surfaces were treated with 2-methyl-labeled [^{14}C]N-2,4-dimethylphenyl-N'-methylformamidine (BTS 27271, purity 95%, specific activity 12.8 ÌCi/mg, Schering Agrochemicals Ltd.), dissolved in acetone, at ca.0.82 kg/ha (which the study author stated was equivalent to an application rate of 1.48 kg of "totally hydrolyzed" amitraz per hectare). The columns were covered with glass filter plates, wrapped for protection from light, and eluted with a total of ca.200 mm (ca.8 inches of deionized water for two days.

The leachate was collected after one and two days, and aliquots were analyzed for total radioactivity by LSC. It was stated that TLC analysis of the leachate was not conducted because of the low concentration of radioactive residues.

After leaching, the soil columns were divided into 2-, 5-, or 10-cm segments. Soil from each segment was extracted in methanol and centrifuged. The extracted soil was air-dried, ground to a fine powder, and analyzed for total radioactivity by LSC following combustion. Aliquots of the methanol extracts were concentrated on a rotary evaporator and analyzed for total radioactivity by LSC; aliquots that contained 1000 dpm of extracted material were analyzed by TLC. The TLC analyses were conducted on silica gel plates developed in cyclohexane:ethyl acetate:diethyl amine (5:3:2) and n-hexane:triethyl amine (17:3). Following development, areas of radioactivity were located and quantified using a TLC linear analyzer. The reported detection limits were 0.17% of the applied for LSC analysis of the leachate, 0.11% of the applied for LSC analysis of the soil extracts, and 0.08-0.42% of the applied for LSC analysis of combusted soil.

DATA EVALUATION RECORD

STUDY 9

CHEM 106201 Amitraz 163-2

FORMULATION--12--EMULSIFIABLE CONCENTRATE (EC)

STUDY ID 40780518
Leake, C.R. 1988b. (W86) The volatilization of [^{14}C]-amitraz from soil under laboratory conditions. Laboratory Project ID ENVIR/88/1. Unpublished study prepared by Schering Agrochemicals Limited, Essex, England, and submitted by Nor-Am Chemical Company, Wilmington, DE.

DIRECT REVIEW TIME = 12

REVIEWED BY: K. Patten TITLE: Staff Scientist

EDITED BY: J. Harlin TITLE: Staff Scientist

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SIGNATURE:

CONCLUSIONS:

Mobility - Laboratory Volatility

This study is acceptable and fulfills EPA Data Requirements for Registering Pesticides by providing information on the volatility of [^{14}C]amitraz (formulated as a 20% EC) from sand soil under laboratory conditions. Volatility of amitraz and its degradates at 25C was: 2.6 x 10^{-6} mm Hg for parent; 2.6 x 10^{-5} for BTS 27919, 9.0 x 10^{-4} for BTS 27271, and 0.2 for BTS 24868. Also detected in the soil was BTS 28037. See p. 9.13 for structures of degradates.

SUMMARY OF DATA BY REVIEWER:

[^{14}C]Amitraz volatilization was minimal from sand soil treated with

phenyl-labeled [^{14}C]amitraz (formulated as a 20% EC) at ca.1.55 kg ai/ha and incubated in the dark at 15 or 30C and 15-60% of the soil moisture holding capacity for 17-18 days. At 17-18 days, 0.1% of the applied amitraz had been evolved at 15C and 0.9 had been evolved at 30C.

Total [^{14}C]residue volatilization in the 15C samples at 18 days post-treatment was 1.9% of the applied for the treated soils regardless of soil moisture holding capacity (15 or 60%) and air flow rate through the flask (100 mL or 1 L per minute). In the 30C samples at 17 days post-treatment, total volatilization was 3.2-4.4% for soils incubated at an air flow of 100 mL/minute regardless of moisture content; 10.7-10.9% for soils incubated at an air flow of 1 L/minute and 45% of the soil moisture holding capacity; and 14.0-20.9% for soils incubated at an air flow of 1 L/minute and 15% of the soil moisture holding capacity. The major volatile degradate was . . .

2,4-dimethylaniline (BTS 24868);

$^{14}CO_2$ was also detected. The registrant-calculated average concentration of BTS 24868 in the air (30C, 15% of moisture holding capacity, 1 L/minute air flow) was 0.0031 ug/cm^2/hour or 2.29 ug/m^3 during the study period.

2,4-Dimethylformanilide (BTS 27919) and

N-2,4-dimethylphenyl-N'-methylformamidine (BTS 27271)

were the major nonvolatile degradates;

2,4-dimethylaniline (BTS 24868) and

N-2,4-dimethyl-N'-(2,4-dimethylphenyl)formamidine (BTS 28037)

were also detected in the soil. The material balances during the study ranged from 86.1 to 101.7% of the applied.

DISCUSSION:

1. Vapor pressures, at 25 C, were reported to be: amitraz, 2.6 x 10^{-6} mm Hg; BTS 27919 2.6 x 10^{-5} mm Hg; BTS 27271, 9.0 x 10^{-4}; and BTS 24868, 0.2 mm Hg.

MATERIALS AND METHODS

MATERIALS AND METHODS:

Sieved (2-mm) sand soil (Typic Udipsamment; ≈91% sand, ≈5% silt, 4% clay, 0.38-0.48% organic matter, pH 7.2-7.3, CEC 3.7-4.5 meq/100 g) was transferred (100-g dry soil equivalent) into 250 mL Erlenmeyer flasks, adjusted to 15, 45, or 60% of moisture holding capacity, and treated with 125 µL of uniformly ring-labeled [^{14}C]amitraz (formulated as a 20% EC, radiochemical purity >96.3%, specific activity 142 µCi/mg, Amersham International) at a rate equivalent to 1.55 kg ai/ha. The soil was sampled immediately after treatment to establish the application rate. The flasks were attached to a continuous air-flow system; humidified, CO_2-free air was drawn sequentially through the sample flask head space, a polyurethane foam bung, one tube of ethanediol, one tube of 0.1 M H_2SO_4, and one tube of ethanolamine. The following treatment combinations were studied:

- 15 ± 2°C, 15% of the soil moisture holding capacity, air flow rate 100 mL/minute;
- 15 ± 2°C, 15% of the soil moisture holding capacity, air flow rate 1 L/minute;
- 15 ± 2°C, 60% of the soil moisture holding capacity, air flow rate 100 mL/minute;
- 15 ± 2°C, 60% of the soil moisture holding capacity, air flow rate 1 L/minute;
- 30 ± 2°C, 15% of the soil moisture holding capacity, air flow rate 100 mL/minute;
- 30 ± 2°C, 15% of the soil moisture holding capacity, air flow rate 1 L/minute;
- 30 ± 2°C, 45% of the soil moisture holding capacity, air flow rate 100 mL/minute; and
- 30 ± 2°C, 45% of the soil moisture holding capacity, air flow rate 1 L/minute.

The flasks were incubated in the dark for up to 18 days. The air flow rate and moisture content of the soils was checked regularly. The polyurethane foam bung and the liquid trapping solutions were replaced with fresh materials periodically. Duplicate flasks from each treatment were removed for analysis at 1, 7, and 17-18 days posttreatment.

The polyurethane foam bungs were extracted three times with cold methylene chloride; the extracts were combined and analyzed by LSC. The foam bungs from the 30°C treatments were further extracted with methylene chloride under hot Soxhlet conditions and the extracts were analyzed by LSC (however, no additional radioactivity was recovered). The ethanediol trapping solutions were analyzed directly by HPLC. The acid trapping

solutions were analyzed for specific [^{14}C]residues (analytical method not specified). The ethanolamine trapping solutions were analyzed for total radioactivity by LSC and for $^{14}CO_2$ by barium chloride precipitation.

The soil samples were Soxhlet-extracted sequentially with methylene chloride for 18 hours and acetonitrile:water (4:1) for 18 hours. Aliquots of the extracts were analyzed for total radioactivity by LSC. The methylene chloride extracts were further analyzed using TLC on silica gel plates developed in cyclohexane:ethyl acetate:triethylamine (5:3:2, v:v:v) and hexane:triethylamine (85:15, v:v). The extracts were cochromatographed with reference standards. After development, the unlabeled standards were located by UV-visualization; the [^{14}C]residues were located using a TLC linear analyzer and autoradiography. Radioactive areas on the plates were scraped, residues were eluted from the silica gel with methanol, and the methanol was analyzed by TLC. The acetonitrile:water extracts were further analyzed by HPLC with UV- and radiodetection. The extracted soil was air-dried and analyzed for unextractable radioactivity by LSC following combustion.

DATA EVALUATION RECORD

STUDY 10

CHEM 106201 Amitraz 164-1

FORMULATION--12--EMULSIFIABLE CONCENTRATE

STUDY ID 40798004
Manley, J.D. and P.J. Snowdon. 1987. (W80) Residues of amitraz and metabolites in soil following orchard treatment with the 20% EC formulation in Texas, USA, 1983/84. Laboratory Project ID RESID/86/132. Unpublished study prepared by Schering Agrochemicals Limited, Essex, England, and submitted by Nor-Am Chemical Company, Wilmington, DE.

DIRECT REVIEW TIME = 16

REVIEWED BY: J. Harlin TITLE: Staff Scientist

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CONCLUSIONS:

Field Dissipation - Terrestrial

This study is scientifically sound and provides supplemental information on the field dissipation of amitraz. The study does not fulfill EPA data requirements for registering pesticides because the analytical methodology was not provided for review, samples were stored frozen but freezer storage stability data were not provided, the soils were incompletely characterized, and field test data were incomplete.

The study indicated a half-life for parent of <<one day and for degradates/residues half-lives were 110 days (BTS 27271), 150 days BTS 27919), and 450 days (total residues). The degradate BTS 27271 was </= 0.04 ppm in 8-12 inch core up to 364 days; BTS 27919 declined to <0.02 ppm in 4-8 inch cosre by 0-14 days.

SUMMARY OF DATA BY REVIEWER:

Amitraz (20% EC) degraded with a half-life of <<1 day to . . .

N-2,4-dimethylphenyl-N'-methylformamidine (BTS 27271) and

2,4-dimethylformanilide (BTS 27919)

in sandy clay loam soil located in grapefruit orchards in Cameron, Texas. The foliage of the grapefruit trees was treated with amitraz at 1.5 lb ai/A/application once or three times (in spring, or spring, summer, and fall, respectively).

In the plot treated once with amitraz, the concentration of BTS 27271 was variable in the upper 4 inches of soil, decreasing from a maximum mean concentration of 0.25 ppm at 0 day posttreatment to 0.07 ppm at 273 days and <0.02 ppm (nondetectable) at 364 days. BTS 27271 was <0.04 ppm in the 4- to 8-inch depth and <0.03 ppm in the 8- to 12-inch depth at intervals up to 364 days posttreatment. BTS 27919 residues in the upper 4 inches of soil decreased from a mean concentration of 0.09 ppm immediately posttreatment to <0.02 ppm at 7-28 days. In the 4- to 8-inch soil depth, BTS 27919 residues were <0.02 ppm at 0-14 days posttreatment. The registrant-calculated half-life for BTS 27271 was 100 days, and for BTS 27271 plus BTS 27919 was 130 days.

In the plot treated with three applications of amitraz, the concentration of BTS 27271 was variable in the upper 4 inches of soil. Following the third application of amitraz, BTS 27271 increased from 0.08 ppm immediately posttreatment to 0.13 ppm at 7 days, then decreased to 0.04 ppm at 273 days and <0.02 ppm at 366 days posttreatment. In the 4- to 8- and 8- to 12-inch depths, BTS 27271 was <0.05 ppm at all sampling intervals following the third application. BTS 27919 was <0.02 ppm at all sampling intervals at all depths following the third application of amitraz. The registrant-calculated half-lives were 110 days for BTS 27271, 150 days for BTS 27271 plus BTS 27919, and 450 days for total amitraz residues.

In pretreatment soil samples from the two plots, BTS 27271 and BTS 27919 were 0.02 ppm in all samples (except once, for BTS 27919 at 0.036 ppm in the 8- to 12-inch depth). During the study, air temperatures ranged from 19 to 104½F and rainfall totaled 25.14 inches.

DISCUSSION:

1. The analytical methods were referenced and were not provided for review. The following methods were referenced:

   Manley, J.D., Snowdon, P.J., FBC Report RESID/86/86 (July 1986). "Analytical Method for Residues of Amitraz in Soil." Registration reference Amitraz/W78;

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Manley, J.D., Snowdon, P.J., FBC Report RESID/86/60 (June 1986). "Analytical Method for Residues for BTS 27271 in Soil." Registration reference Amitraz/W76;

Manley, J.D., Snowdon, P.J., FBC Report RESID/86/61 (June 1986). "Analytical Method for Residues of BTS 27919 in Soil." Registration reference Amitraz/W77; and

Manley, J.D., Snowdon, P.J., FBC Report RESID/86/52 (June 1986). "Analytical Method for Combined Residues of Amitraz and Metabolites in Soil". Registration reference Amitraz/W75.

2. Soil samples were stored frozen at -20 C for an unspecified period of time prior to analysis; however, freezer storage stability data were not provided.

3. The soils were not completely characterized. The textural analyses (percent sand, silt and clay) and CECs were not reported.

4. Field test data were incomplete. The slope of the field and depth to the water table were not reported. Soil temperature data were only provided for the application dates. Meteorological data were incomplete; air temperature and rainfall data, provided on a monthly basis, did not include information for the month of June 1983, when the study was initiated.

5. Field maintenance practices during the study were not described.

6. In the original document, the study authors compiled the residue data from the three sampling depths into one composite sample for each sampling interval. However, individual soil samples taken from incremental soil depths should be analyzed and reported separately in order to determine the extent of leaching. Since the data provided in Tables 15-19 of Appendix VI (pages 70-77) report residue data for each sampling depth and therefore, more accurately reflect the extent of leaching, data from these tables were used by the reviewer to summarize the results of the study.

7. The study authors stated that amitraz degraded immediately to the degradates BTS 27271 and BTS 27919 following single or multiple applications of the 20% EC formulation; it was not possible to confirm the application rate since no parent compound was present at the first sampling interval. Based on an aerobic soil metabolism study (Study 4), amitraz degrades with a half-life of <1 day, which is in agreement with the results reported in this field dissipation study.

8. The study authors suggested that the variable nature of the residues in the soil was a result of treating the tree foliage rather than the soil, causing an uneven distribution of amitraz on the soil surface.

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9. In the original document, Table 18 of Appendix VI (pages 74-75) stated to contain residue data for degradate BTS 27919; however, the table was mislabeled to read "BTS 27271 residue level" rather than "BTS 27919 residue level".

10. An additional experiment was conducted to determine the laboratory degradation of [^{14}C]amitraz in soil. Following application of [^{14}C]-amitraz to 50-g soil samples at 1.04 ug/ml, amitraz degraded rapidly to the degradates BTS 27271 and BTS 27919.

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MATERIALS AND METHODS

MATERIALS AND METHODS:

Amitraz (20% EC, BFC Chemicals, Inc.) was applied at 1.5 lb ai/A/application once (5/6/83) or three times (5/6/83, 7/8/83, and 10/4/83; total 4.5 lb ai/A) to separate grapefruit orchard plots (each plot 3375 ft^2) of sandy clay loam soil (1.0% organic matter, pH 7, soil not further characterized) located in Cameron, Texas. The pesticide was applied to the tree foliage using a high speed orchard sprayer. Soil samples (0- to 4-, 4- to 8-, and 8- to 12-inch depths) were taken from each plot prior to treatment and at intervals up to 364-366 days posttreatment (including 0, 7, 14, and 28 days posttreatment). Samples were stored at -20°C until analysis.

The majority of samples were analyzed without further drying due to the rapid degradation of amitraz. In some cases, to ensure representative sampling, a portion of each soil sample was partially dried to facilitate grinding, sieved (2 mm), and refrozen prior to analysis. Soil samples were analyzed using referenced analytical methods that were summarized but not provided in detail to review. In order to determine the concentration of amitraz in the soil (FBC Report RESID/86/86), the soil samples were extracted with acetone and filtered; the acetone was removed by rotary evaporation and analyzed by GLC with sensitive thermionic specific detection. In order to determine the concentration of N-2,4-dimethylphenyl-N'-methylformamidine (BTS 27271) in the soil (FBC Report RESID 86/60), the soil samples were extracted with toluene:aqueous sodium hydroxide by shaking. The soils were centrifuged, and the toluene phase was removed. The toluene extracts were then partitioned into aqueous acetic acid, made alkaline (pH not specified), and back partitioned into toluene. The toluene extract was analyzed using GLC with sensitive thermionic specific detection. In order to determine the concentration of 2,4-dimethylformanilide (BTS 27919) in the soil (FBC Report RESID/-86/61), the soil samples were Soxhlet-extracted with toluene. Toluene was removed from the extract by rotary evaporation, and the extract was filtered through a silica minicolumn and analyzed by GC with sensitive thermionic specific detection. Total amitraz metabolites in the soil were quantified using a referenced analytical method (FBC Report RESID/-86/52). All "components" were base hydrolysed to 2,4-dimethylaniline (BTS 24868), which was simultaneously extracted into toluene by steam distillation. Extracts were partitioned into acid and back partitioned between base and toluene. Total BTS 24868 residues were determined by GC with sensitive thermionic specific detection. Reported recoveries were 70-97% for soil samples fortified with amitraz at 0.02-0.40 ppm; 76-107% for samples fortified with BTS 27271 at 0.01-1.0 ppm; 73-99% for samples fortified with BTS 27919 at 0.01-0.20 ppm; and, 78-102% for samples fortified with total metabolites at 0.01-0.20 ppm. The detection limit was 0.02 ppm for amitraz and its degradates.

DATA EVALUATION RECORD

STUDY 11

CHEM 106201 Amitraz 165-4

FORMULATION--00--ACTIVE INGREDIENT

STUDY ID 00072503
Mastone, J.D. and M.E. Barrows. 1981. Accumulation and elimination of ^{14}C residues by bluegill sunfish (Lepomis macrochirus) exposed to ^{14}C-labeled amitraz. METAB/81/11. Report No. BW-80-10-760. Unpublished study prepared by EG & G Bionomics and submitted by Nor-Am Chemical Company, Wilmington, DE.

STUDY ID 40780519
Lines, D. 1981. (W14) The examination of residues of bluegill sunfish (Lepomis macrochirus) exposed to ^{14}C amitraz. Laboratory Project ID METAB/81/36. Unpublished study prepared by Schering Agrochemicals Limited, Essex, England, and submitted by Nor-Am Chemical Company, Wilmington, DE.

DIRECT REVIEW TIME = 8

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STUDY ID 40780519 is an addendum to STUDY ID 00072503, which was previously reviewed in 1984. Detailed information from the review of STUDY ID 00072503 is presented in this report, in addition to modifications presented in STUDY ID 40780519.

CONCLUSIONS:

Laboratory Accumulation - Fish

This study may be acceptable if the source of the degradates (specific fish tissue) is provided. It was unclear whether the degradate analysis

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data were for a single tissue type (muscle, viscera, or carcass) or were averaged from all three tissue types. Maximum bioaccumulation factors were ca. 280X for muscle, 2118X for viscera, 1467X for carcass, and 933X for whole fish. Major degradates in fish tissue were BTS 27919 and BTS 27271.

SUMMARY OF DATA BY REVIEWER:

Total [^{14}C]amitraz residues accumulated in bluegill sunfish with maximum bioconcentration factors of ca. 280x, 2118x, 1467x, and 933x in muscle, viscera, carcass, and whole fish tissues, respectively, during 30 days of exposure to [^{14}C]amitraz residues (purity 99.7%) at ca. 0.01 ppm in a flow-through system. Maximum concentrations of [^{14}C]residues were 4.2 ppm in muscle tissue (day 30), 36.0 ppm in visceral tissue (day 10), 22.0 ppm in carcass tissue (day 30), and 14.0 ppm in whole fish (day 30). Of the [^{14}C]amitraz residues in muscle tissue sampled on day 21 of the exposure period, 19% were hexane-extractable, 36% were methanol-extractable, and 45% were not extractable with either solvent. After 14 days of depuration, [^{14}C]residues were 0.5 ppm in muscle tissue, 4.2 ppm in visceral tissue, 3.8 ppm in carcass tissue, and 1.9 ppm in whole fish. Total [^{14}C]residues (uncharacterized) in the treated water were 0.011-0.018 ppm during the exposure period.

Based on further analysis of the 21-day (exposure) treated fish, the distribution of total [^{14}C]residues in the various fish tissues was 18.1% in muscle, 16.8% in viscera, and 65.1% in carcass. In the 21-day samples (it was not specified which tissue or tissues the data were obtained from), 46% of the total radioactivity was methanol/hexane/water extractable:

2,4-dimethylformanilide (BTS 27919)

comprised 18.0% of the total radioactivity,

N-2,4-dimethylphenyl-N'-methylformamidine (BTS 27271)

comprised 7.4%, polar extractables comprised 8.5%, and unidentified compounds comprised 12.6%. In some extracts the unidentified compounds appeared to cochromatograph with 4-formamido-m-toluic acid (BTS 39098), 4-amino-m-toluic acid (BTS 28369), and 2,4-dimethylaniline (BTS 24868); however, according to the study author, extremely low concentrations of each unknown made positive identification impossible.

DISCUSSION:

1. Although the study author indicated that three tissue types (muscle, viscera, and carcass) were extracted for degradate identification, only one set of values were presented. It could not be determined if the results from the three tissue types were averaged or if in fact only one tissue type was fully characterized.

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2. Data from analyses of untreated water and fish were not provided.

MATERIALS AND METHODS

MATERIALS AND METHODS:

(Study ID 00072503)

Bluegill sunfish (Lepomis macrochirus, average weight and length, 63 ± 3 mm and 3.4 ± 0.6 g, respectively) were maintained at 20 ± 1° C for ≥14 days prior to the initiation of the study. Flow-through aquatic exposure systems were prepared using two 3-L aquaria equipped with continuous-flow proportional dilution apparatus. Aerated well water (pH 6.6, dissolved oxygen 6.7 ppm, alkalinity 24 ppm as $CaCO_3$, hardness 23 ppm as $CaCO_3$, temperature 22°C) was provided to each aquarium as a rate of 8 turnovers per day.

Bluegill sunfish (150) were placed in each aquarium, and one aquarium was continuously treated with [^{14}C]amitraz (BTS-27419; purity 99.7%, specific activity 2174 dpm/μg, The Boots Company) at 0.01 ppm. The second aquarium served as an untreated control. Following a 30-day exposure period, fish remaining in the [^{14}C]amitraz-treated aquarium were transferred to an aquarium containing untreated water for a 14-day depuration period. During the exposure period, water and fish samples were taken on days 1, 3, 7, 10, 14, 22, and 30; during the depuration period, fish samples were taken on days 1, 3, 7, 10, and 14. Fish were frozen until analysis.

Water samples were analyzed for total radioactivity using LSC. The fish were divided into muscle, visceral, and carcass tissues, and subsamples were air-dried and analyzed for total radioactivity using LSC following combustion. Additional edible tissue from fish sampled on day 21 of exposure was homogenized with hexane followed by methanol. The extracts were concentrated and analyzed for total radioactivity using LSC. The extracted tissue was analyzed for unextractable radioactivity using LSC following combustion. Recovery values ranged from 99 to 101%. Detection limits were 0.003-0.004 ppm for water and 0.007-0.62 ppm for fish tissue.

(Study ID 40780519)

In order to identify specific [^{14}C]degradates in the fish, subsamples of muscle, visceral, and carcass tissues from the 21-day (exposure) treated and control fish were analyzed. Pooled samples of each tissue type were freeze-dried, then homogenized sequentially with hexane, methanol, and water. The samples were centrifuged after each extraction, and the supernatants were concentrated under a stream of nitrogen. The extracted tissues were dried, mixed with glucose, and analyzed for unextractable radioactivity by LSC following combustion. Total radioactivity in the hexane, methanol, and water extracts was quantified by LSC. The hexane and methanol extracts were further analyzed by TLC on silica gel plates developed in cyclohexane:ethyl acetate:triethylamine (50:30:20), diethyl ether:triethylamine (95:5), or chloroform:methanol:acetic acid (100:7.5:-1). Reference compounds were cochromatographed with the samples, and following development, were visualized under UV light. Radioactive areas were located with a TLC radioscanner and quantified LSC.

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