Shaughnessy No.: 106201

Date Out of EFGWB: 9/10/91

To: Mr. Dennis Edwards
Product Manager # 12
Registration Division (TS-767)

From: Paul Mastradone, Ph.D., Chief
Environmental Chemistry Review Section #1
Environmental Fate & Ground Water Branch/EFED (H7507C)

Thru: Henry Jacoby, Chief
Environmental Fate & Ground Water Branch/EFED (H7507C)

Attached, please find the EFGWB review of...

Reg./File #: 45639-RUA

Chemical Name: Amitraz

Type Product: Miticide

Product Name: MITAC EC OVASYN

Company Name: NOR-AM Chemical Company

Purpose: Review of aerobic aquatic metabolism study, fish accumulation study, supplemental soil photolysis data, foliar dissipation study protocol, supplemental batch equilibrium data, and data requirements for indoor greenhouse/ornamental plant use category.

Action Code: 181/177 EFGWB #(s): 900518/900637/900785
Date Received 5/88 Total Reviewing Time: 15 days

Deferrals to: ___ Ecological Effects Branch

___ Dietary Exposure Branch

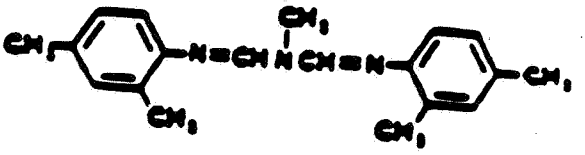
___ Non-Dietary Exposure Branch

___ Toxicology Branch I

___ Toxicology Branch II

1.0 CHEMICAL:

chemical name: N,N'-[(Methylimino)-dimethylidyne]-di-2,4-xyline
common name: Amitraz
trade name: OVAYSN, Mitac, Taktic, Triatox
structure:



CAS #:
Shaughnessy #:106201

2.0 TEST MATERIAL: discussed in DER

3.0 STUDY/ACTION TYPE:

Review of aerobic aquatic metabolism study, fish accumulation study, additional information on soil photolysis and adsorption-desorption studies, foliar dissipation study protocol, and data requirements for indoor greenhouse/ornamental use category.

4.0 STUDY IDENTIFICATION:

Paul, Paula. 1990. Protocol: Dissipation of Residues of Amitraz, BTS 27271, and BTS 27919 on Cotton Foliage. Submitted and sponsored by NOR-AM Chemical Company, Wilmington DE.

Allen, R. 1989. The fate of [14C]-amitraz following repeated applications in a sediment/water 'microcosm'. Submitted and sponsored by NOR-AM Chemical Company, Wilmington DE. Performed by Schering Agrochemicals Limited, Essex England. Received by EPA 4/4/90. MRID 414442-05.

Brehm, M. 1989. (W85 Addendum) The photodegradation of amitraz (Schering Code No. ZK 49974) on soil surfaces. Submitted and sponsored by NOR-AM Chemical Company, Wilmington DE. Performed by Schering AG, Berlin West Germany. Received by EPA 4/4/90. MRID 414442-04.

Barrett, K. L. and A. E. Lattimore. 1990. (W111) Determination of the accumulation and elimination of [14C]-amitraz bluegill sunfish (Lepomis machrochirus). Submitted and sponsored by NOR-AM Chemical Company, Wilmington DE. Performed by Schering Agrochemicals Limited, Essex England. Received by EPA 4/4/90. MRID 414442-06.

Vukich, Jacob 1990. Application for Registration of OVERTURE EC. Submitted and sponsored by NOR-AM Chemical Company, Wilmington DE.

Allen, R. 1990. Addendum I to (W83): The Adsorption Equilibria of Amitraz in Sand, Sandy Loam, Clay Loam and Clay Soils. Submitted and sponsored by NOR-AM Chemical Company, Wilmington DE.

5.0 REVIEWED BY:

James A. Hetrick, Ph.D.
Chemist, ECRS # 1
EFGWB/EFED/OPP

Signature: James G. Hetrick
Date: SEP 10 9[illegible]

6.0 APPROVED BY:

Paul Mastradone, Ph.D.
Section Chief, ECRS # 1
EFGWB/EFED/OPP

Signature: Paul J. Mastradone
Date: SEP 10 9[illegible]

7.0 CONCLUSIONS:

7.1 Status of Data Requirements:

Data Requirements		Review Status
Hydrolysis	(161-1)	- Partially[1]
Aqueous photolysis	(161-2)	- Partially[1]
Soil photolysis	(161-3)	- Partially[1]
Air photolysis	(161-4)	- Not Satisfied
Aerobic soil metabolism	(162-1)	- Partially[1]
Anaerobic soil metabolism	(162-2)	- Not Satisfied
Aerobic aquatic metabolism	(162-4)	- Not Satisfied
Leaching/adsorption/desorption	(163-1)	- Partially[1]
Laboratory volatility	(163-2)	- Satisfied
Field volatility	(163-3)	- Not Satisfied
Terrestrial field dissipation	(164-1)	- Not Satisfied
Long-term field dissipation	(164-5)	- Reserved
Confine crop accumulation	(165-1)	- Not Satisfied
Field crop accumulation	(165-2)	- Partially
Fish accumulation	(165-4)	- Not Satisfied
Nontarget aquatic organism accumulation	(165-5)	- Reserved

1- Partially satisfied indicates the data requirement has been fulfilled for parent amitraz.

7.2 GENERAL: EFGWB has reviewed the fate data in support of a greenhouse/non-food crop use pattern. At this time, the environmental fate studies [Hydrolysis, Aerobic Soil Metabolism, Leaching and Adsorption/Desorption, Laboratory Volatility] provide acceptable fate data for parent amitraz; however, the environmental fate studies provide little or no environmental fate data for the BTS 27,271, BTS 27,919, and BTS 24,868 (Please refer to Section 7.8).

Based on the current environmental fate data, EFGWB believes the use of Overature EC in a greenhouse/nonfood crop use patterns should cause minimal environmental exposure to amitraz and its degradates. In theory, pesticide use in greenhouses would restrict amitraz applications to confined areas with controlled drainage. Therefore, EFGWB believes the environmental exposure to amitraz and its degradates probably would be of little environmental concern.

7.3 The aerobic aquatic metabolism study (MRID# 41444205) is scientifically sound and provides supplemental information for the 162-4 data requirement. At this time, the study cannot be fully evaluated without the following information:

1. The limit of detection (LOD) and limit of quantification (LOQ) for parent amitraz and its degradates are required to confirm the validity of the reported data.

2. Recovery studies for amitraz and its degradates are required to validate extraction efficiency from sediment and water samples.

Based on supplemental data, parent amitraz in an aerobic aquatic ecosystem rapidly hydrolyzes ($t_{1/2}$= 1.4-3.2 hours) to form 2,4-dimethylformanilide (BTS 27,919) and N-2,4-dimethylphenyl-N-methylformamidine (BTS 27,271). These degradates were more persistent than parent amitraz; for example, the half-lives of BTS 27,919 and BTS 27,271 were estimated at 10 days and 53 days, respectively. The degradates, BTS 27,919 and BTS 27,271, hydrolyzed to form 2,4-dimethylaniline (BTS 24,868) and BTS 28,037. Thereafter, BTS 24,868 and BTS 28,037 were slowly mineralized ($t_{1/2}$ ≈ 28 days) with subsequent residue incorporation into nonlabile (bound) organic matter.

The data suggest that parent amitraz is less persistent than its hydrolytic degradates in aerobic aquatic ecosystems.

7.4 The fish accumulation study (MRID# 41444206) is scientifically sound and provides supplemental information for the 164-5 data requirement. At this time, the study cannot be fully evaluated without the following information:

1. The [^{14}C]-residues should be identfied and quantified using appropiate analytical methods.

2. Provide a storage stability study to confirm the stability of amitraz and its hydrolytic degradates in fish tissue matrices.

Based on supplemental information, parent amitraz has an estimated bioaccumulation factor of 1821X in the viscera, 588X in the flesh, and 1838X in the carcess of bluegill. During a 14 day depuration period, the bioaccumulated [^{14}C]-amitraz residues (92% of the bioaccumulated residues) were depurated from whole fish tissue.

The reported data suggest that amitraz residues can accumulate in fish tissue; however, the bioaccumulated amitraz residues appear to be eliminated during depuration.

7.5 <u>General:</u> A foliar dissipation study (132-2) is not a data requirement of the EFGWB; instead, it is administered by the Non-dietary Exposure Branch (NDEB). The review of the proposed foliar dissipation study is restricted for use by EFGWB/EEB and has no bearing on the guideline acceptability of the study.

The proposed foliar dissipation study does not appear to be adequately designed to measure the dissipation rates of amitraz and its degradates. EFGWB believes the study design does not provide sufficient replication to obtain reliable statistics. A minimum of 4 replicates may be necessary to measure the foliar dissipation of amitraz and its hydrolytic degradates. In addition, EFGWB recommends that cotton leaves should be sampled in reference to plant height (cm above ground) to compensate for a pesticide deposition gradient. This sampling scheme should provide a reasonable measure of the foliar pesticide concentration without imposing significant sample variability.

7.6 The soil photolysis study (Brehm, 0407805[illegible] in conjunction with additional information (Brehm, 41444204) partially fulfills the 161-3 data requirement. This data requirement will be fulfilled with submission of the soil photolytic half-lives for the major hydrolytic degradates, i.e., 2,4-dimethylformanilide (BTS 27,919), N-2,4-dimethylphenyl-N-methylformamidine (BTS 27,271), and 2,4-dimethylaniline (BTS 24,868) . (Please refer to Section 10.2 for more details on the additional information of the soil photolysis study.)

7.7 The batch equilibrium study (MRID# 40780515) in conjunction with the estimated K_{ad} for parent amitraz satisfy the unaged residue portion of the adsorption/desorption-leaching (163-1) data requirement.

Based on acceptable data, the K_{ad} for parent amitraz was 1.69 (1/n= 0.53) in Shelford loamy sand, 3.01 (1/n= 0.76) in Speyer sand, 89.13 (1/n=1.22) in Terling clay loam, and 16.31 (1/n=0.75), , in a Shelford Field clay soil. Parent amitraz, therefore, appears to be mobile in sandy soil with low organic matter contents (< 1.72% O.M.) and immobile in heavier textured soils.

7.8 Environmental Fate Assessment:

Based on supplemental and acceptable environmental fate data from the 1987 Amitraz Registration Standard to present, parent amitraz degradation is dependent on hydrolysis. The rate of hydrolysis was dependent upon solution pH; the hydrolysis rate was inversely related to the pH of the medium. Amitraz hydrolysis was faster in slightly acidic environments ($t_{1/2}$ = 2 hours) than in alkaline environments ($t_{1/2}$ = 25.5 hours). In aerobic mineral soil, parent amitraz had a half-life of less than one day. The amitraz degradates formed during aerobic soil metabolism were as follows: BTS 27271 (≈13%), BTS 27919 (≈35%), BTS 24868(≈13%), and CO_2 (≈35%). Similarly, parent amitraz had a field dissipation half-life of less than a day. Parent amitraz, therefore, appears to be extremely unstable in terrestrial and aquatic ecosystems.

The amitraz degradates, BTS 27271, and BTS 27919, are formed through hydrolytic degradation of parent amitraz. Based on supplemental data, parent amitraz in an aerobic aquatic ecosystem rapidly dissipated ($t_{1/2}$= 1.4-3.2 hours) to form 2,4-

dimethylformanilide (BTS 27,919) and N-2,4-dimethylphenyl-N-methylformamidine (BTS 27,271). These degradates were more persistent than parent amitraz; for example, the half-lives of BTS 27,919 and BTS 27,271 were estimated at 10 days and 53 days, respectively. The degradates, BTS 27,919 and BTS 27,271, hydrolyzed to form 2,4-dimethylaniline (BTS 24,868) and BTS 28,037. Thereafter, BTS 24,868 and BTS 28,037 were slowly mineralized ($t_{1/2}$ ≈ 28 days) with subsequent residue incorporation into nonlabile (bound) organic matter. In field studies, the rate of degradate dissipation can only be approximated by field dissipation data; the half-life was 110 and 150 days for BTS 27271 and BTS 27919, respectively.

8.0 RECOMMENDATIONS:

8.1 Inform the registrant the environmental fate data to support a greenhouse use pattern are satisfied. Although environmental fate data for the major degradates is incomplete, EFGWB believes that greenhouse uses of amitraz will restrict the release of parent amitraz and degradates into the environment.

8.2 Inform the registrant the aerobic aquatic metabolism study (MRID 41444204) is scientifically sound and provides supplemental data. This study cannot be fully evaluated without aa a complete description of analytical detection limits (e.g., LOD and LOQ), and extraction efficiencies for parent amitraz and its hydrolytic degradates in soil and water matrices. Upon receipt of the requested information, the study will be reevaluated for its fulfillment of the 163-4 data requirement.

8.3 Inform the registrant that the fish accumulation study (MRID 41444206) is scientifically sound and provides supplemental data. This study cannot be fully evaluated because amitraz residue identification was not confirmed by two analytical methods and the storage stability of amitraz residues in fish tissue matrices is unknown. If the registrant can provide confirmatory identification of the [^{14}C]-residues and storage stability data for the amitraz residues then EEFGW will reevaluate the study for its fulfillment of the 164-5 data requirement.

8.4 Inform the registrant the proposed foliar dissipation study does not appear to be designed to adequately measure foliar pesticide degradation rates. EFGWB believes that 2 field replications are insufficient to provide reliable data for estimating a foliar dissipation rates. In addition, EFGWB suggest that cotton leaf samples should be taken as a function of plant height to reduce sample variability.

8.5 Inform the registrant the additional information on analytical detection limits (Brehm, 414442-04) provides the necessary data to validate previously submitted soil photolysis data (Brehm,00407805). (Please refer to Section 10.2 for more details.)

8.6 Inform the registrant the batch equilibrium study (MRID# 40780515) in conjunction with the estimated Freundlich K_{ad}s for parent amitraz satisfy the unaged residue portion of the adsorption/desorption-leaching (163-1) data requirement.

9.0 BACKGROUND:

10.0 DISCUSSION OF INDIVIDUAL TESTS OR STUDIES:

10.1 GENERAL: A foliar dissipation study (132-2) is not a data requirement of the EFGWB; instead, it is administered by Non-Dietary Exposure Branch. The review of the proposed foliar dissipation study design is restricted for use by EFGWB/EEB and has no bearing on the guideline acceptability of the study.

NOR-AM Chemical Company has submitted an experimental protocol to determine the foliar dissipation of parent amitraz and its hydrolytic degradates on cotton. The field studies will be conducted in the major cotton producing areas, e.g., California, Arizona, Florida, and Texas, under both irrigated and nonirrigated conditions. The experimental treatments will consist of a control, single application of OVASYN (1.5 EC) at a rate of 0.5 ug a.i. kg^{-1} (1 lb.ai/acre), and four application intervals (7 days apart) of OVASYN (1.5 EC) at a rate of 0.125 ug a.i. kg^{-1} (0.25 lbs ai/acre).

Within each treatment, cotton leaf samples will be taken at 2 hours post-treatment, 1, 3, 7, 14, 21, and 28 days post pesticide treatment. At each sampling interval, approximately 1 kg of cotton leaves will be taken from 10 plants at four different plant positions. Each treatment will have 2 replications to allow for calculation of a mean and standard deviation.

EFGWB believes that the proposed study design does not provide sufficient replication to obtain reliable statistics. A minimum of 4 replicates may be necessary to adequately determine the foliar dissipation. In addition, EFGWB recommends that cotton leaves should be sampled in reference to plant height (cm above ground) to compensate for a pesticide deposition gradient. This sampling scheme should provide a reasonable measure of the foliar pesticide concentration without imposing significant sample variability.

10.2 General: In the 1987 Amitraz Registration Standard, the soil photolysis study (Brehm, 00407805) was accepted and fulfilled the 163-3 data requirement. Upon further review, the study was considered supplemental pending submission of the analytical detection limits for parent amitraz and its hydrolytic degradates.

The supplemental soil photolysis data (Brehm, 41442-04) indicate the HPLC sensitivity was 0.298 counts/dpm. The limit of detection (3σ) for HPLC radio-chromatograms was measured at 320 dpm (≈ 1.7% of total ^{14}C), 447 dpm (≈ 2.3% of total ^{14}C), and 197 dpm (≈ 1.0% of total ^{14}C) for BTS 27,919, BTS 27217, and parent amitraz, respectively. The limit of quantification (10σ) for radiochromatograms was measured at 509 dpm (≈ 2.7% of total ^{14}C),

713 dpm (≈ 3.7% of total ^{14}C), and 769 dpm (≈ 4.0% of total ^{14}C) for BTS 27,919, BTS 27217, and parent amitraz, respectively.

The reported data in the soil photolysis study (Brehm,00407805) was consistently greater than the reported LOQ. Therefore, the analytical methods were sufficient to determine the soil concentration of parent amitraz and its hydrolytic degradates.

10.3 The batch equilibrium study (MRID # 40780515) did not fulfill the unaged residue portion of the 163-1 data requirement because amitraz adsorption was described by distribution coefficients (K_d). EFGWB believes that distribution coefficients (K_d) may not adequately describe amitraz adsorption; the use of distribution coefficients (K_d) assumes a linear relationship for parent amitraz adsorption on soil. Therefore, EFGWB requested that Freundlich adsorption coefficients (K_{ad}) be estimated from the submitted adsorption data.

NOR-AM Response: NOR-AM estimated parent amitraz adsorption at equilibrium concentrations of 1 $\mu g\ ml^{-1}$ and 1 $\mu g\ L^{-1}$. NOR-AM warns the adsorption coefficients (K_{ad}) were estimated by extrapolation and may not provide reliable partitioning coefficients (K_d). More importantly, NOR-AM recommends that estimation of amitraz adsorption using the K_{ad} requires the proper distribution factor (1/n).

The K_{ad} for parent amitraz was estimated at 1.69 (1/n= 0.53) in a Shelford loamy sand, 3.01 (1/n= 0.76) in a Speyer sand, 89.13 (1/n=1.22) in a Terling clay loam, and 16.31 (1/n=0.75) in a Shelford Field clay soil. Therefore, amitraz appears to be mobile in sandy soil with low organic matter contents (< 1.72% O.M.) and immobile in clay soils.

EFGWB Response: EFGWB recognizes the problems of estimating Freundlich K_{ad}s when the pesticide concentration is less than 1 $\mu g\ ml^{-1}$; the estimation error for Freundlich coefficients are magnified and undefined by data extrapolation. However, the estimated adsorption coefficients (K_{ad}) provide adsorption data at a constant amitraz solution concentration of 1 $\mu g\ ml^{-1}$.

EFGWB concludes the batch equilibrium study (MRID# 40780515) in conjunction with the estimated K_{ad} for parent amitraz satisfy the unaged residue portion of the adsorption/desorption-leaching (163-1) data requirement.

11.0 COMPLETION OF ONE-LINER:
12.0 CBI APPENDIX: N/A

Environmental Fate & Effects Division
PESTICIDE ENVIRONMENTAL FATE ONE LINE SUMMARY
AMITRAZ
Last Update on September 20, 1991
[V] = Validated Study [S] = Supplemental Study [U] = USDA Data

LOGOUT	Reviewer:	Section Head:	Date:

Common Name:AMITRAZ
PC Code # :106201 CAS #:33089-61-1 Caswell #:

Chem. Name :N'-(2,4-DIMETHYLPHENYL)-N-{{(2,4-DIMETHYLPHENYL)IMINO}-METHYL}-N-METHYLMETHANIMIDAMIDE
Action Type:INSECTICIDE/ACARICIDE

Trade Names:
(Formul'tn):EC (20% AND 12.5%); WP 50%
Physical State:

Use Patterns (% Usage) :VEY EFFECTIVE IN THE CONTROL OF PEAR PSYLLA ON PEARS, :WHITEFLY ON COTTON, AN ALSO AGAINST TETRANYCHID AND ERIO- :PHYID MITES ON FRUIT, CITRUS, ORNMENTALS. :

Empirical Form: $C_{19}H_{23}N_3$
Molecular Wgt.: 293.41 Vapor Pressure: 2.60E -6 Torr
Melting Point : °C Boiling Point: °C
Log Kow : pKa: @ °C
Henry's : E Atm. M3/Mol (Measured) 1.00E -6 (calc'd)

Solubility in ...				Comments
Water	1.00E	ppm @	°C	
Acetone	E	ppm @	°C	
Acetonitrile	E	ppm @	°C	
Benzene	E	ppm @	°C	
Chloroform	E	ppm @	°C	
Ethanol	E	ppm @	°C	
Methanol	E	ppm @	°C	
Toluene	E	ppm @	°C	
Xylene	E	ppm @	°C	
	E	ppm @	°C	
	E	ppm @	°C	

Hydrolysis (161-1)
[V] pH 5.0: 2.1 HOURS
[V] pH 7.0:22.1 HOURS
[V] pH 9.0:25.5 HOURS
[ ] pH :
[ ] pH :
[ ] pH :

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Photolysis (161-2, -3, -4)
[S] Water:7 HRS IN Hg ARC LAMP
[ ] :
[ ] :
[ ] :

[V] Soil :<30 MINUTES
[ ] Air :

Aerobic Soil Metabolism (162-1)
[V] <1 DAY IN SiLm AND SdLm SOILS
[S] 6-12 WEEKS IN LOAM AT 21-26 C
[ ] AND 12% MOISTURE.
[S] 2-4 HOURS IN 2 JAPANESE SOILS
[ ]
[ ]
[ ]

Anaerobic Soil Metabolism (162-2)
[ ]
[ ]
[ ]
[ ]
[ ]
[ ]
[ ]

Anaerobic Aquatic Metabolism (162-3)
[ ]
[ ]
[ ]
[ ]
[ ]
[ ]
[ ]

Aerobic Aquatic Metabolism (162-4)
[S] Parent amitraz t1/2 = 1.4 to 3.2 hours
[ ] BTS 27919 t1/2 = 10 days
[ ] BTS 27271 t1/2 = 53 days
[ ] BTS 24868 t1/2 = 28 days
[ ] BTS 28037 t1/2 = 28 days
[ ]
[ ]

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Soil Partition Coefficient (Kd) (163-1)
[V] Parent amitraz: Shelford loamy sand-Kf=1.69 (1/n= 0.53)
[ ] Speyer sand-Kf=3.01 (1/n=0.76)
[ ] Terling clay loam-Kf=89.13 (1/n=1.22)
[ ] Shelford clay-Kf= 16.31 (1/n=0.75)
[ ] Note: Soil names are derived from British Soil Taxonomy
[ ]

Soil Rf Factors (163-1)
[V] AGED RESIDUES WERE MOBILE IN
[ ] Sd, SdLm, AND ClLm SOILS
[S] 0.36 - 0.48 IN SdLm TO CLAY;
[ ] 0.91 IN SAND.
[ ]
[ ]

Laboratory Volatility (163-2)
[ ]
[ ]

Field Volatility (163-3)
[ ]
[ ]

Terrestrial Field Dissipation (164-1)
[S] T1/2 FOR PARENT COMPOUND = << 1 DAY IN SdClLm SOIL IN
[ ] TEXAS; FOR DEGRADATE BTS 27271 IT WAS 110 DAYS, FOR BTS
[ ] 27919 IT WAS 150 DAYS.
[ ]
[ ]
[ ]
[ ]
[ ]
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[ ]

Aquatic Dissipation (164-2)
[ ]
[ ]
[ ]
[ ]
[ ]
[ ]

Forestry Dissipation (164-3)
[ ]
[ ]

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Long-Term Soil Dissipation (164-5)
[ ]
[ ]

Accumulation in Rotational Crops, Confined (165-1)
[ ]
[ ]

Accumulation in Rotational Crops, Field (165-2)
[ ]
[ ]

Accumulation in Irrigated Crops (165-3)
[ ]
[ ]

Bioaccumulation in Fish (165-4)
[S] BLUEGILL SUNFISH BCF: 280 X FOR MUSCLE, 2118 X FOR VISCERA,
[ ] AND 933 X FOR WHOLE FISH.

Bioaccumulation in Non-Target Organisms (165-5)
[ ]
[ ]

Ground Water Monitoring, Prospective (166-1)
[ ]
[ ]
[ ]
[ ]

Ground Water Monitoring, Small Scale Retrospective (166-2)
[ ]
[ ]
[ ]
[ ]

Ground Water Monitoring, Large Scale Retrospective (166-3)
[ ]
[ ]
[ ]
[ ]

Ground Water Monitoring, Miscellaneous Data (158.75)
[ ]
[ ]
[ ]

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Field Runoff (167-1)
[ ]
[ ]
[ ]
[ ]

Surface Water Monitoring (167-2)
[ ]
[ ]
[ ]
[ ]

Spray Drift, Droplet Spectrum (201-1)
[ ]
[ ]
[ ]
[ ]

Spray Drift, Field Evaluation (202-1)
[ ]
[ ]
[ ]
[ ]

Degradation Products

BTS 27919 (volatility = 2.6E-5) is major degradate
BTS 24868 (volatility = 2E-1)

Koc= 1000 estimate

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Comments

Soil Koc = 1000 (estimate, U)
Photolysis half-lives in sunlight days of summer and fall range from 3.27 days to 26.4 days.
Volatility values range from 3.8E-7 to 2.6E-6.
After leaching 32-cm SdLm columns with 22.5 cm of .01 M CaCl2,20% of appl radioact. was bound to the soil in the 2.5 cm soil segment adjacent to the treated segment, and 3.5% was in the remainder of the soil column.
Bioaccumulation in Fish- 1821X in viscera, 588X in flesh, and 183X in carcess of bluegill. The bioaccumulated residues were eliminated over 14 day depuration period.

References: EPA REVIEWS
Writer : PJH JAH

DATA EVALUATION REVIEW

I. Study Type: Fish Accumulation Study

II. Citation: Barrett, K. L. and A. E. Lattimore. 1990. (W111) Determination of the accumulation and elimination of [14C]-amitraz bluegill sunfish (Lepomis machrochirus). Submitted and sponsored by NOR-AM Chemical Company, Wilmington DE. Performed by Schering Agrochemicals Limited, Essex England. Received by EPA 4/4/90. MRID 414442-06.

III. Reviewer:

Name: James A. Hetrick, Ph.D., Chemist James A. Hetrick
Title: Environmental Chemistry Review Section #1
Organization: EFGWB/EFED/OPP

IV. Approved by:

Name: Paul J. Mastradone, Ph.D., Chief Paul J Mastradone
Title: Environmental Chemistry Review Section #1
Organization: EFGWB/EFED/OPP

V. Conclusions:

This study is scientifically valid and provides supplemental information for the 164-5 data requirement. At this time, the study cannot be fully evaluated without the following information:

1. The [^{14}C]-residues should be identified and quantified using at least two analytcial methods. TLC chromatograms do not indicate a clear separation of the degradates, BTS 24868 and BTS 279191. EFGWB believes poor TLC residue separation prevents confirmatory identification by co-chromatographic techniques.

2. Provide a storage stability study to confirm the chemical stability of amitraz and its hydrolytic degradates in fish tissue matrices.

Based on supplemental information, parent amitraz has an estimated bioaccumulation factor of 1821X in the viscera, 588X in the flesh, and 1838X in the carcass bluegill tissues. During depuration, the [^{14}C]-amitraz residues were eliminated from whole fish tissue.

These data suggest that parent amitraz can accumulate in fish tissue; however, the bioaccumulated residues are eliminated during depuration.

VI. Materials and Methods:

Pesticide Exposure Phase

One-hundred and seventy four juvenile bluegill sunfish (average weight of 0.824 grams and length of 39.28 mm) were placed into glass exposure vessels containing 142 L of pesticide amended water. Each of the exposure vessels had an amitraz concentration of 20 ug L^{-1}. The concentration of amitraz in water was maintained constant by continuous replenishment with a stock [^{14}C]-amitraz solution (0.02 mg amitraz (specific activity 253 uCi mg^{-1}, radiopure 96.7%) ml^{-1} pumped at rate of 100 ug ml min^{-1}) to compensate for a system flow rate of 1 L min^{-1} (Figure 1). The exposure vessels were maintained at a temperature of 22°C.

At specified sampling intervals, fish were removed from each exposure vessel for analysis of bioaccumulated residues; six fish were taken at 1, 3, 7, 10, 14, 17, 19, and 21 days after initiating the experiment. In addition, a one liter subsample of exposure solution was taken to determine the water physicochemical properties, e.g., pH, conductivity, hardness, and alkalinity. at each sampling period.

Depuration Phase

After the 21 day pesticide exposure period, fifty fish were transferred from each exposure vessel to a glass depuration vessels containing pesticide-free water. At specified sampling intervals, fish were removed from each exposure vessel for analysis of bioaccumulated residues; six fish were taken at 1, 3, 7, 10, and 14 day intervals after the transfer date.

Analytical

The fish were dissected and separated into flesh (skin), viscera (alimentary tract and associated internal organs), and carcass (fins, head, and gills) tissue. Each of the fish tissues (flesh, viscera, and carcass) were sequentially extracted with dichloromethane and methanol to remove soluble [^{14}C]-amitraz residues. Thereafter, the extracted fish tissue was combusted to determine the quantity of bound [^{14}C]-amitraz residues.

The [^{14}C]-amitraz residues in fish tissue extracts were separated by TLC . Reverse-phase TLC was conducted on fish extracts using three different solvent systems: methanol\water, chloroform \ethylacetate, chloroform\ethylacetate\ammonia. In contrast, [^{14}C]-amitraz residues in the exposure solution were separated by HPLC. The HPLC separation was conducted using an acetonitrile :phosphate solvent system through a Dynamac C18 column (10x250mm) coupled to a Hitachi UV detector (wavelength 254 nm) and a LBK betacord radioactive monitor. The separated compounds were identified by co-chromatographic comparison with standard compounds. The [^{14}-C] content in extracts and exposure solutions was determined by LSC.

VII. Study Author's Results and/or Conclusions:

A. Amitraz accumulation in fish tissue reached a plateau after 21 days of pesticide exposure (Figure 5; Appendix IV).

B. The average bioaccumulation factor for parent amitraz was estimated at 1821X, 588X, and 1838X in the viscera, flesh, and carcass tissues, respectively.

C. The distribution of [^{14}C]-amitraz residues in fish tissue was as follows: 71% (18 mg kg^{-1}) in the carcass, 19.8% (12 mg kg^{-1}) for flesh, and 9.2% (32 mg kg^{-1}) for viscera (Table 4). Please note that amitraz concentrations are expressed as amitraz equivalents per wet weight of fish tissue.

D. The flesh and viscera tissues had trace quantities (≤ 4% of bioaccumulated ^{14}C) of parent amitraz BTS 27,271, BTS 27919, and NC 24868. In contrast, the carcass tissue had measurable concentrations (≥ 10% of bioaccumulated ^{14}C) of BTS 27,271, parent amitraz, and BTS 27,919 (Tables 5 and 6).

E. During a 14 day depuration period, the [^{14}C]-amitraz residues (92% of the bioaccumulated residues) were eliminated from fish tissue.

Reviewer Comments:

A. The TLC chromatograms indicate that the degradates, BTS 24868 and BTS 27919, were poorly separated with the different solvent systems (Figures 5,6,and 7). EFGWB believes that the TLC separation resolution does not allow for quantification of BTS 24,868 and BTS 27,919. More importantly, the [^{14}C]-residues should be identified and quantified using at least two analytcial methods.

DATA EVALUATION REVIEW

I. Study Type: Aerobic Aquatic Metabolism

II. Citation: Allen, R. 1989. The fate of [14C]-amitraz following repeated applications in a sediment/water 'microcosm'. Submitted and sponsored by NOR-AM Chemical Company, Wilmington DE. Performed by Schering Agrochemicals Limited, Essex England. Received by EPA 4/4/90. MRID 414442-05.

III. Reviewer:

Name: James A. Hetrick, Ph.D., Chemist James A Hetrick SEP 10
Title: Environmental Chemistry Review Section #1
Organization: EFGWB/EFED/OPP

IV. Approved by:

Name: Paul J. Mastradone, Ph.D., Chief Paul J Mastradone
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V. Conclusions:

This study is scientifically sound and provides supplemental information for the 162-4 data requirement. At this time, the study cannot be fully evaluated without the following information:

1 The limit of detection (LOD) and limit of quantification (LOQ) for parent amitraz and its degradates are required to confirm the validity of the reported data.

2 There are no recovery studies for amitraz and its degradates to validate extraction efficiency from sediment and water samples.

Based on supplemental data, parent amitraz rapidly hydrolyzes ($t_{1/2}$= 1.4-3.2 hours) to form 2,4-dimethylformanilide (BTS 27,919) and N-2,4-dimethylphenyl-N-methylformamidine (BTS 27,271). These degradates are more persistent than parent amitraz; for example, the half-lives of BTS 27,919 and BTS 27,271 were estimated at 10 days and 53 days, respectively. The degradates, BTS 27,919 and BTS 27,271, hydrolyze to form 2,4-dimethylaniline (BTS 24,868) and BTS 28,037. Thereafter, BTS 24,868 and BTS 28,037 are slowly mineralized ($t_{1/2} \approx$ 28 days) with subsequent residue incorporation into nonlabile (bound) organic matter.

The data suggest that parent amitraz is less persistent than its hydrolytic degradates in aerobic aquatic ecosystems.

VI. Materials and Methods:

The "microcosm" study was conducted with sediment and water taken from the River Granta, Essex, England. Physicochemical properties of the sediment are shown in Table 1.

Each of the microcosms consisted of a glass column (4.5 cm diameter x 30 cm height) loosely packed with 350 cc of sediment covered with 750 ml of river water (Figure 1). The "microcosms" were maintained under aerobic conditions by bubbling CO_2-free laboratory air into the water phase. In addition, each microcosm was connected with volatility traps containing ethanediol and ethanlamine to retain organic volatiles and CO_2, respectively. The microcosms were incubated at a temperature of 25 +/-2°C.

Each of the microcosms was treated with parent amitraz (radiolabeled amitraz 96.6% radiopure, specific activity 138.05 uCi mg^{-1}) at a rate of 0.45 lbs a.i./A every 10 days for the first 20 days of the experiment. Water and sediment samples were taken from each microcosm at 0, 1, 3, 6, 10, 11, 13, 16, 20, 21, 23, 26, 30, and 59 days after the first pesticide application. In addition, replicated "microcosms" were maintained to allow for measurement of insitu sediment redox potential and water pH.

Analytical

Sediment samples were sequentially extracted with dichloromethane and acetonitrile:water (80:20 v/v). The acetonitrile:water extracts were further solvent partitioned with dichloromethane. The aqueous portion of the dicloromethane partition was acidified (pH-1) and further solvent partitioned in ethyl acetate.

The separation of [^{14}C]-amitraz residues was accomplished by HPLC and TLC. The HPLC separation was conducted using an acetonitrile :phosphate carrier through a Dynamac C18 column (10x250 mm) coupled to a Merc-Hitachi C-4000 UV detector and a Betacord radioactivity UV monitor. In addition, TLC separations were conducted using the following solvent systems: ether/hexane /triethylamine, ether /triethylamine, toluene/trimethylamine, and chloroform /methanol/acetic acid. The separated compounds were identified by co-chromatographic comparison with standard compounds. The quantity of [^{14}C]-amitraz residues was measured by LSC.

The dissipation rate of parent amitraz and its hydrolytic degradates was determined using kinetic based models (Appendix VII).

VII. Study Author's Results and/or Conclusions:

A. Within each microcosm, the material balance accounted for 90 to 99% of the applied [^{14}C]-amitraz (Table 4).

B. After 59 days of incubation, the [^{14}C]-amitraz residues were distributed between various phases: namely, aqueous phase (≈13%),

sediment bound (≈8%), unextractable (≈50%), and volatile organic (≈2%), and CO_2 (≈10%) (Table 4).

C. In the aqueous phase, parent amitraz dissipated rapidly ($t_{1/2}$= 1.4 hours using a 2 compartment model) due to hydrolysis. Similarly, parent amitraz in a sediment/water matrix rapidly dissipated ($t_{1/2}$ = 3.2 hours using a 3 compartment model) due to soil adsorption and hydrolysis (Figures 3 and 4, Table 5).

D. The residues formed from amitraz degradation were BTS 27,919 (form-2',4'-xylidide), BTS 27,271 (N-methyl-N'-(2,4-xylyl)formamidine), BTS 24868 (2,4 dimethylaniline), and BTS 28037 (N,N'-bis(2,4-xylyl)formamidine) (Tables 5 and 6).

E. The degradate, BTS 27,919, had a maximum concentration in the aqueous phase (≈ 40% of applied [^{14}C]-amitraz) after a 3 day incubation period. The dissipation half-life of BTS 27,919 in both aqueous and sediment/water phases was estimated at ≈ 10 days using a 1 compartment kinetic model (Appendix VIII, Figure 3).

F. The degradate, BTS 27,271, had a maximum concentration in the aqueous phase (≈ 4% of applied [^{14}C]-amitraz) after a 24 hour incubation period. The aqueous dissipation half-life of BTS 27,271 was estimated at ≈ 29 hours using a 2 compartment kinetic model. In contrast, the sediment/water dissipation half-life of BTS 27,271 was estimated at ≈ 53 days (Appendix VIII, Figure 3).

G. The degradate, BTS 24868, had a constant concentration (≈ 7% of applied [^{14}C] -amitraz) in the aqueous phase over a 30 day incubation period. The dissipation half-life for BTS 24868 in aqueous and sediment phases was estimated at ≈ 28 days using a 1 compartment kinetic model (Appendix VIII, Figure 3).

H. Several unidentified degradates were isolated in the aqueous phase (≈ 10.5% of the total [^{14}C]-amitraz) (Tables 5 and 6).

I. The volatile degradates were identified as BTS 24868(≈ 2% of applied ^{14}C-amitraz) and CO_2 (≈ 10% applied ^{14}C-amitraz).

Reviewer Comments:

A. The analytical detection limits for parent amitraz and its hydrolytic degradates are not presented in the study. More importantly, there were no recovery studies for amitraz and its hydrolytic degradates from soil and water matrices. EFGWB believes that the analytical detection limits and recovery studies are necessary to validate the observed data.

B. The reviewer appreciates the registrant's effort to report redox potentials. This measurement is seldom, if ever, reported in metabolism studies.