Shaughnessy No.: 106201
Date Out of EFGWB: DEC - 6 1989

TO: Dennis Edwards
Product Manager # 12
Registration Division (TS-767)

FROM:

Paul Mastradone, Ph.D., Section Chief
Environmental Chemistry Review Section #1
Environmental Fate and Groundwater Branch

THRU:

Henry Jacoby, Chief
Environmental Fate and Groundwater Branch
Environmental Fate and Effects Division (H7507C)

Attached please find the EFGWB review of:

Reg./File # : 45639-49, 45639-RUA, 45639-EUP-UL

Chemical Name: Amitraz

Product Type : Miticide

Product Name : MITAC EC, Ovasyn

Company Name : NOR-AM Chemical Company

Purpose : Review data submitted to support registration of use on cotton and for experimental use permit on apples

Date received: 2/27/89, 8/29/89, 9/28/89

Action Code: 161, 759
EFGWB No. 90387, 90738, 90790

Total Reviewing Time (decimal days): 6.0

Deferrals to:
_____Ecological Effects Branch, EFED
_____Science Integration & Policy Staff, EFED
_____Non-Dietary Exposure Branch, HED
_____Dietary Exposure Branch
_____Toxicology Branch, HED

Date Received 9/25/89

OFFICE OF PESTICIDE PROGRAMS DATA REVIEW RECORD 49719 ATTACHMENT 1 EFED

Confidential Business Information-Does Not Contain National Security Information(E.O. 12065)
This form is to be used for individual studies and for submission of pesticide applications

1. PRODUCT NAME | CHEMICAL NAME Amitraz

2. IDENTIFYING NUMBER	3. RECORD NUMBER	4. ACTION CODE	5. MRID/ACCESSION NUMBER	6. STUDY GUIDELINE OR NARRATIVE
4F3437-439	252304	161		Photolysis in pH 7 buffer

7. REFERENCE NUMBER	8. DATE RECEIVED (EPA)	9. PRODUCT/REVIEW MANAGER/DCI	10. PM/RM TEAM NUMBER	11. DATE SENT TO (HED/EFED/RD/BEAD)
		EDWARDS	12	9/27/89
12. PROJECTED RETURN DATE 10/27/89	13. DATE RETURNED TO (RD/SRRD) 12/15/89	INSTRUCTIONS: Please review the attached submission from Nor-Am regarding the absorption-excretion study & photolysis study.		

(THIS SECTION APPLIES TO REVIEW OF STUDIES ONLY)

14. CHECK APPLICABLE BOX:

☐ ADVERSE 6(a)(2) DATA (405)
☐ SPECIAL REVIEW DATA (870)
☐ GENERIC DATA (REREGISTRATION) (660)
☐ PRODUCT SPECIFIC DATA (REREGISTRATION) (655)

15. NUMBER OF INDIVIDUAL STUDIES SUBMITTED ____

16. HAVE ANY OF THE ABOVE STUDIES (in whole or in part) BEEN PREVIOUSLY SUBMITTED FOR REVIEW? (circle: yes or no) IF YES, PLEASE IDENTIFY THE STUDY(IES):

17. RELATED ACTIONS:

18.	TO	TYPE OF REVIEW	19. REVIEWS ALSO SENT TO	20. DATA REVIEW CRITERIA
HED		SCIENCE ANALYSIS & COORD.	SAC, PC	A. Policy Note #31
		TOXICOLOGY/HFA	TOX/HFA, PL	☐ 1 = data which meet 6(a)(2) or meet 3(c)(2)(B) flagging criteria
		TOXICOLOGY/IR	TOX/IR	☐ 2 = data of particular concern from registration standard
		DIETARY EXPOSURE	DEB, EA	☐ 3 = data necessary to determine tiered testing requirements
		NON-DIETARY EXPOSURE	NDE, AC	B. Section 18
EFED	✓	ECOLOGICAL EFFECTS	BA	☐ 1 = data in support of section 3 in lieu of section 18
	✓	ENVIRONMENTAL FATE & GROUND H2O	EEB, EFGWB	C. Inert Ingredients
SRRD		SPECIAL REVIEW		☐ 1 = data in support of continued use of List 1 inert
		REREGISTRATION		
		GENERIC CHEMICAL SUPPORT	SR, RER, GSC	
RD		INSECTICIDE-RODENTICIDE		
		FUNGICIDE-HERBICIDE		
		ANTIMICROBIAL		
		PRODUCT CHEMISTRY	IR, FH	
		PRECAUTIONARY LABELING	AM	
BEAD		ECONOMIC ANALYSIS		
		ANALYTICAL CHEMISTRY		
		BIOLOGICAL ANALYSIS		

☐ CONFIDENTIAL STATEMENT OF FORMULA (TRADE SECRETS) ☐ LABEL ATTACHED

White - Data Coordinator
Yellow - Data Review Section
Pink - PM/RM/DCI
Green - Return with completed review
Include original + two (2) copies with each submission

374A

Tack No. 49047
Date Received 3/27/89

ATTACHMENT 1

OFFICE OF PESTICIDE PROGRAMS DATA REVIEW RECORD

Confidential Business Information-Does Not Contain National Security Information(E.O. 12065)
This form is to be used for individual studies and for submission of pesticide applications

1. PRODUCT NAME			CHEMICAL NAME	
OVASYN			AMITRAZ	
2. IDENTIFYING NUMBER	3. RECORD NUMBER	4. ACTION CODE	5. MRID/ACCESSION NUMBER	6. STUDY GUIDELINE OR NARRATIVE
45639-RUA	239936	160	40999905-09	165-2
9F03730	240811	241		

7. REFERENCE NUMBER	8. DATE RECEIVED (EPA)	9. PRODUCT/REVIEW MANAGER/DCI	10. PM/RM TEAM NUMBER	11. DATE SENT TO (HED/EFED/RD/BEAD)
	02/9/89	Edwards/Garrola	12	02/27/8

12. PROJECTED RETURN DATE	13. DATE RETURNED TO (RD/SRRD)
04/27/89	12/15/89

INSTRUCTIONS: This is a new registration request. NOR. AM wishes to register Amitraz for use on cotton. Please review the registration

(THIS SECTION APPLIES TO REVIEW OF STUDIES ONLY)

14. CHECK APPLICABLE BOX:

15. NUMBER OF INDIVIDUAL STUDIES SUBMITTED ____

☐ ADVERSE 6(a)(2) DATA (405) ☐ SPECIAL REVIEW DATA (870) ☐ GENERIC DATA (660) (REREGISTRATION) ☐ PRODUCT SPECIFIC DATA (65 (REREGISTRATION)

16. HAVE ANY OF THE ABOVE STUDIES (in whole or in part) BEEN PREVIOUSLY SUBMITTED FOR REVIEW? (circle: yes or no) IF YES, PLEASE IDENTIFY THE STUDY(IES):

17. RELATED ACTIONS:

18.	TO	TYPE OF REVIEW	19. REVIEWS ALSO SENT TO	
HED		SCIENCE ANALYSIS & COORD.	SAC	PC
		TOXICOLOGY/HFA	TOX/HFA	PL
		TOXICOLOGY/IR	TOX/IR	
		DIETARY EXPOSURE	DEB	EA
		NON-DIETARY EXPOSURE	NDE	AC
EFED	✓	ECOLOGICAL EFFECTS		BA
		ENVIRONMENTAL FATE & GROUND H2O	EEB	
SRRD		SPECIAL REVIEW	EFGWB	
		REREGISTRATION		
		GENERIC CHEMICAL SUPPORT	SR	
RD		INSECTICIDE-RODENTICIDE	RER	
		FUNGICIDE-HERBICIDE	GSC	
		ANTIMICROBIAL		
		PRODUCT CHEMISTRY	IR	
		PRECAUTIONARY LABELING	PH	
BEAD		ECONOMIC ANALYSIS	AM	
		ANALYTICAL CHEMISTRY		
		BIOLOGICAL ANALYSIS		

☐ CONFIDENTIAL STATEMENT OF FORMULA (TRADE SECRETS) ☐ LABEL ATTACHED

20. DATA REVIEW CRITERIA

A. Policy Note #31
☐ 1 = data which meet 6(a)(2) or meet 3(c)(2)(B) flagging criteria
☐ 2 = data of particular concern from registration standard
☐ 3 = data necessary to determine tiered testing requirements

B. Section 18
☐ 1 = data in support of section 3 in lieu of section 18

C. Inert Ingredients
☐ 1 = data in support of continued use of List 1 inert

White - Data Coordinator

Pink - PM/RM/DCI

Date received

49630
ATTACHMENT 1
EFED
8-29-89

OFFICE OF PESTICIDE PROGRAMS DATA REVIEW RECORD

Confidential Business Information-Does Not Contain National Security Information(E.O. 12065)
This form is to be used for individual studies and for submission of pesticide applications

1. PRODUCT NAME — CHEMICAL NAME: Amitraz

2. IDENTIFYING NUMBER	3. RECORD NUMBER	4. ACTION CODE	5. MRID/ACCESSION NUMBER	6. STUDY GUIDELINE OR NARRATIVE
15639-EUP-UL	249465	750		

7. REFERENCE NUMBER	8. DATE RECEIVED (EPA)	9. PRODUCT/REVIEW MANAGER/DCI	10. PM/RM TEAM NUMBER	11. DATE SENT TO (HED/EFED/RD/BEAD)
		EDWARDS	12	8/25/89

12. PROJECTED RETURN DATE	13. DATE RETURNED TO (RD/SRRD)	INSTRUCTIONS:
11/25/89	12/15/89	Please review proposed Amitraz apple EUP

(THIS SECTION APPLIES TO REVIEW OF STUDIES ONLY)

14. CHECK APPLICABLE BOX:

15. NUMBER OF INDIVIDUAL STUDIES SUBMITTED [ ]

☐ ADVERSE 6(a)(2) DATA (405)
☐ SPECIAL REVIEW DATA (870)
☐ GENERIC DATA (660) (REREGISTRATION)
☐ PRODUCT SPECIFIC DATA (655) (REREGISTRATION)

16. HAVE ANY OF THE ABOVE STUDIES (in whole or in part) BEEN PREVIOUSLY SUBMITTED FOR REVIEW? (circle: yes or no) IF YES, PLEASE IDENTIFY THE STUDY(IES):

17. RELATED ACTIONS:

18. TO	TYPE OF REVIEW
	SCIENCE ANALYSIS & COORD.
	TOXICOLOGY/HFA
	TOXICOLOGY/IR
	DIETARY EXPOSURE
	NON-DIETARY EXPOSURE
	ECOLOGICAL EFFECTS
X	ENVIRONMENTAL FATE & GROUND H2O
	SPECIAL REVIEW
	REREGISTRATION
	GENERIC CHEMICAL SUPPORT
	INSECTICIDE-RODENTICIDE
	FUNGICIDE-HERBICIDE
	ANTIMICROBIAL
	PRODUCT CHEMISTRY
	PRECAUTIONARY LABELING
	ECONOMIC ANALYSIS
	ANALYTICAL CHEMISTRY
	BIOLOGICAL ANALYSIS

19. REVIEWS ALSO SENT TO

__ SAC __ PC
__ TOX/HFA __ PL
__ TOX/IR
__ DEB __ EA
__ NDE __ AC
__ BA
__ EEB
__ EFGWB
__ SR
__ RER
__ GSC
__ IR
__ FH
__ AM

20. DATA REVIEW CRITERIA

A. Policy Note #31
☐ 1 = data which meet 6(a)(2) or meet 3(c)(2)(B) flagging criteria
☐ 2 = data of particular concern from registration standard
☐ 3 = data necessary to determine tiered testing requirements

B. Section 18
☐ 1 = data in support of section 3 in lieu of section 18

C. Inert Ingredients
☐ 1 = data in support of continued use of List 1 inert

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☐ LABEL ATTACHED

White - Data Coordinator
Yellow - Data Review Section
Pink - PM/RM/DCI
Green - Return with completed review
Include original + two (2) copies with each submission

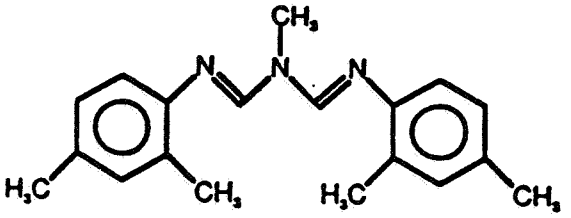
1.0 CHEMICAL:

Common Name- Amitraz

Chemical Name- N,N'-[(Methylimino)-dimethylidyne]-di-2,4-xylidine

Trade Name- Mitac, Taktic, Triatox

Structure-



2.0 TEST MATERIAL: ^{14}C-Amitraz

3.0 STUDY/ACTION TYPE:

Review submitted rotational crop study, aqueous photolysis study and response to previous EFGWB review of the batch equilibrium adsorption study.

Consider studies in support of registration of amitraz for use on cotton and for an experimental use permit (EUP) for use on apples.

4.0 STUDY IDENTIFICATION:

Castro, L. 1988. Residues of amitraz and its major metabolites in soil and rotational crops following application of MITAC EC to cotton; Lab Project #12010; NOR-AM Chemical Co.; Exton, PA. Accession #409995-09.

Allen, R. and C. I. Keller. 1989. Response to EPA Review of Amitraz Adsorption/Desorption Study (W83); MRID No. 40780515. NOR-AM Chemical Company. MRID No. 412067-04.

Brehm, A. 1988. (W101 Addendum) The Photolysis of Amitraz (Shering Code No.ZK 49 974) In Aqueous Solution. Shering Agrochemicals Limited (UK) for NOR-AM Chemical Co. MRID No. 412067-03.

5.0 REVIEWED BY:

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

Signature: James L. Hetrick
Date: 12/6/89

6.0 APPROVED BY:

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

Signature: Paul J Mastradone
Date: DEC - 6 1989

7.0 CONCLUSION:

7.1 EFGWB concludes that adequate data are not available to support the registration of amitraz for use on cotton.

1. The registrant should be alerted to the fact that EFGWB has concerns about the potential of amitraz residues to leach into groundwater when applied to cotton grown in sandy soils. Thus, to support this registration, additional field dissipation study must be conducted where field dissipation and the leaching potential for amitraz and its soil degradates are investigated.

2. Submitted rotational crop data only partially satisfy the requirement for rotational crop study. Only one geographical cotton growing area is represented--the arid southwestern U. S. See Section 7.3, below.

7.2 EFGWB concludes that adequate data are available to support the EUP for use on apples under the submitted experimental program. However, the registrant should be alerted to the fact that EFGWB has concerns about the potential of amitraz residues to leach into groundwater when applied to apple orchards grown in sandy loam, silt loam or clay soils. Thus, to support this registration, an additional field dissipation study must be conducted where field dissipation and the leaching potential for amitraz and its soil degradates are investigated.

Previous EFGWB review dated 7-19-89 and 6-28-89 noted deficiencies in the photolysis on soil, leaching-adsorption and fish accumulation study. Because of these deficiencies, EFGWB concluded that the data did not support the EUP for use on citrus.

This reviewer notes that:

1. The photolysis on soil study is not a requirement for an EUP.

2. There are deficiencies in the leaching-adsorption study. The additional information submitted by the registrant did not make the study acceptable. The K_d values for the study should be calculated and reported. Until this information is submitted, the study is still considered supplemental.

(See Section 7.4, below.)

All the leaching studies reviewed so far have been judged supplemental: (1) A soil column study indicated aged residues were mobile in a Florida sand and an (English) sandy loam (?) soil. (The reviewer questioned the classification.) Radioactive residues were found in the leachates of both columns. (2) Soil thin-layer chromatography study indicated that amitraz residues were intermediately mobile in sandy loam, silt loam and clay soils (R_f 0.36-0.48) and very mobile in sand (R_f 0.91). The radioactive residues were all amitraz degradate BTS-27919

While these studies are judged supplemental, it is doubtful that any additional useful information can be gained by requiring the registrant to repeat these studies for the EUP for use on apples.

3. The fish accumulation study indicated that bluegill sunfish had maximum bioaccumulation factors of ca. 280X for muscle, 2118X for viscera, 1467 for carcass tissues and 933X for whole fish. After a 14 day depuration period, 86% to 89% of the accumulated residues were depurated.

The study was found deficient in that the location of the reported degradates within the fish body (i.e., in which fish tissue or if in whole body) was not supplied. However, the data do indicate that the majority of the residues taken up are depurated when fish are not exposed to amitraz residues.

7.3 Field Rotational Crop Study

EFGWB concludes that the submitted study is acceptable and partially satisfies this data requirement. See attached Data Evaluation Record (DER). The results of the study indicated that Amitraz residues (calculated as total amitraz equivalents) were not detected (>0.05 ppm) in the rotated crops (red beets, cabbage, and wheat) grown in California and planted 44 days after treatment (emergency replant) or 113-155 days after treatment (normal agricultural rotation). Application to the primary cotton crop was at 0.75 lb ai/A (one application) and 1.0 lb ai/A (0.5 lb ai/A two applications).

However, only one geographical cotton growing area--the arid southwestern U. S.--is represented. This is acceptable provided amitraz will not be used in other cotton growing areas of the United States (i.e., the southeastern U. S.) and the label prohibits planting of rotational crops following cotton treated with amitraz in the southeastern U. S. cotton growing area. Otherwise, a rotational crop study representing this area will be required.

EFGWB notes deficiencies in this study:

1. Soil was not sampled at times of planting of the rotational crops or at harvest of the rotational crops. Actual soil sampling was done for a field dissipation protocol and not for the field rotational crop study. However, since no detectable residues (> 0.05 ppm) were found in the soil after one day after application, this deficiency does not effect EFGWB's conclusion.

2. Immature plant parts were not analyzed for those rotational crops which could be harvested or foraged at an immature stage (e.g., winter wheat). However, since the level of residues in the soil were below the limit of detection after one day after application, this deficiency does not effect EFGWB's conclusion.

3. The mature wheat samples were not separated into individual plant parts prior to analysis (i.e., into straw, chaff and grain). However, since no detectable levels of residues were found in the mature wheat samples, this deficiency does not effect EFGWB's conclusion.

4. Rotational crop samples were not analyzed for parent amitraz and the individual metabolites. However, because no residues were found in the rotational crops, this deficiency does not effect EFGWB's conclusion.

7.4 Adsorption/Desorption Study

EFGWB concludes that all the numerous leaching studies reviewed so far have been judged supplemental. The information submitted of the adsorption/desorption study do not resolve the deficieinces noted in the study. Based on this consideration, EFGWB concludes that calculated K_d values should be submitted. See item 3, below.

The registrant has provided responses to the EFGWB comments in the previous review of the adsorption/desorption study:

Allen, R. and C. I. Keller. 1989. Response to EPA Review of Amitraz Adsorption/Desorption Study (W83); MRID No. 40780515. NOR-AM Chemical Company. MRID No. 412067-04.

The original reviewer comment will be given followed by the NOR-AM response then the EFGWB reply:

1. Reviewer comment: The soils were sieved too finely (1 mm), rather than at 2 mm which would increase the clay content and favor adsorption.

Table 3

Soil Properties

Particle size analysis[a]	Shelford (wooded area)	Speyer 2.1	Terling	Shelford field
Coarse sand >600 um	6	7	12	6
sand 210–600 um	47	66	13	15
Fine sand 105–210 um	11	18	2	4
Very find sand 60–105 um	2[f]	2	1	1
Coarse silt 20–60 um	11	3	32	6
Silt 2–20 um	9	2	20	12
Clay <2 um	14	2	20	56
Textural Class[b]	Sandy loam	Sand	*Clay loam **Loam[g]	Clay
Organic carbon (%)[c]	3.3	0.4	3.3	4.4
pH[d]	5.11	5.20	6.34	6.87
Cation exchange capacity[e] (meq/100g)	26.1	3.2	24.6	33.4

(a) Determined by sieving and sedimentation by Ministry of Agriculture Soil Science Department, Cambridge, UK.
(b) *ADAS (British) **USDA (USA) soil classification.
(c) Obtained by Walkley and Black method: Methods of soil analysis edited by C.A. Black et. al.
(d) pH determined with 1:25 soil/solution ratio in 0.01 M $CaCl_2$.
(e) As given in analysis of Agricultural Material HMSO (88,427) 1981.
(f) This value was incorrectly listed as 12 in the original report.
(g) This description was incorrectly listed as Clay in the original report.

NOR-AM response: The use of a 1 mm sieve led to an increased clay content of less than 2%. This increase would have a very minimal affect on adsorption. A re-calculated distribution of the 600-1000 um fraction is as follows:

	Shelford (wooded)	Speyer 2.1	Terling	Shelford Field
Coarse Sand (600-1000 um)	2	2	4	2
Sand (210-600 um)	49	69	14	16
Fine Sand	11.5	19	2	4
V. Fine Sand	2	2	1	1
Coarse Silt	11.5	4	35	6
Silt	9	2	22	13
Clay.	15	2	22	58

EFGWB reply: EFGWB concludes soil that has been sieved to less than 1 mm may alter the soil soil adsorption capacity. According to the USDA-Soil Taxonomy textural classification, very coarse sand comprises the 1 to 2mm particle size fraction; therefore, the removal of this soil fraction may cause improper textural classification, and more importantly, influence the cation exchange capacity (CEC) and related charge of the soil. EFGWB realizes eliminating the very coarse sand fraction will increase amitraz adsorption by concentrating the clay fraction. Furthermore, the actual quantity of clay is probably less important than the type of clay mineral. The effect of using finely-sieved soil is that the soil CEC and related charge (based on soil mass) is higher than a similar soil sieved to less than 2mm. Therefore, EFGWB accepts this deficiency in the adsorption experiments; however, future adsorption experiments should be conducted on soil sieved to pass a 2mm (#10 mesh) screen.

2. Reviewer comment: Desorption as well as adsorption of existing amitraz residues should have been addressed.

NOR-AM response: Since amitraz rapidly decomposes in soil, a desorption study would actually be the same as the aged leaching study which has been accepted by EFGWB. It is NOR-AM's position that a repeat batch study on the parent compound is not necessary.

EFGWB reply: EFGWB accepts the registrant's comment. In this case, a desorption study would be equivalent to the aged leaching study. The soil column aged residue leaching study indicated that amitraz degradates were mobile in the soil. While the majority of the radioactive residues were in the upper 10 cm of the column, the residues were distributed throughout the columns with 1.55%-5.2% of the applied radioactivity was found in the leachate. Similar results were observed in the soil column leaching studies for the two degradates of amitraz (although the studies were

considered supplemental).

3. Reviewer comment: Distribution coefficients were calculated instead of Freundlich K values.

NOR-AM response: The Freundlich K value represents the concentration of pesticide adsorbed to soil colloids at an equilibrium solution concentration of 1 ug/ml. However, in this study the equilibrium solutions concentrations were less than 0.03 ug/ml in all cases. Therefore, to extrapolate data from these concentrations to a much higher concentration in order to determine the Freundlich K value is meaningless.

Kf values may be more appropriate if ug/L and ug/kg units were used instead. These values would now be:

Soil	Kf	1/n	r
Shelford (wooded)	43.1	0.53	0.874
Speyer 2.1	15.8	0.76	0.913
Terling	19.5	1.22	0.930
Shelford Field	91.7	0.75	0.877

EFGWB reply: EFGWB does not consider calculations of the Freundlich K values to be meaningless in this case. Such Freundlich K values are necessary for comparative purposes and should be provided. The reported "Kf" values are ambiguous.

4. Reviewer comment: 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.

NOR-AM response: In order to classify the particle size distribution according to USDA guidelines, a calculation (based on analyses conducted by the UK Ministry of Agriculture) is made where 3/4 of the material in the 20-63 um range (coarse silt) is allocated to the silt fraction and 1/4 to the sand fraction.

There are 2 typographical errors in Table 3.

Shelford (wooded area), Very Fine Sand should be 2%, not 12%.

Terling USDA classification should be Loam, not Clay.

A corrected page is presented herein in response to Reviewer comment 1.

EFGWB comment: EFGWB notes these corrections and amends the review accordingly.

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

NOR-AM response: According to H. D. Chapman, in Methods of Soil Analysis (Black et al.) American Society of Agronomy, pp. 891-901, typical CEC values range from 1-100 meq/100 g. Our soils are, therefore, not atypical, having CEC's in the range of 3-33 meq/100 g.

EFGWB reply: While CEC values may range from 1-100 meq/100 g for the various soil types within the U. S., these values for these soils (CEC = 26.1-33.3 meq/100 g) are higher than those of the soils typical of the intended use areas.

7.5 Aqueous Photolysis Study

EFGWB concludes that the study is scientifically sound and supports the conclusions drawn from the laboratory study.

The registrant has submitted an additional study to support the previously reviewed laboratory aqueous photolysis study. The results of the study indicate that amitraz degraded with half-lives of about 14 hours when exposed to natural sunlight and of about 16 hours in the dark control maintained under similar conditions.

Based on the results of the study, EFGWB concludes that amitraz may degrade in the aqueous environment with a half-life of about 4 days by photolysis alone. However, it appears that hydrolysis as well as photolysis contributed to degradation of amitraz in the aquatic environment. Hydrolysis, in fact, may be the predominant means of dissipation in the aquatic environment.

The previous review indicated that the aqueous photolysis study was unacceptable since the test solutions were not sterilized. In addition, 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 adsorption spectra of amitraz in the test solutions were not provided. This study has some of the same deficiencies. However, EFGWB concludes that little additional information would be gained by requiring the registrant to repeat the study. Thus, taken together, these

studies satisfy the aqueous photolysis data requirement.

8.0 RECOMMENDATION:

8.1 Inform the registrant that the available data are not sufficient to satisfy the environmental fate data requirements for registration of amitraz for use on cotton.

The registrant should be alerted to the fact that EFGWB has concerns about the potential of amitraz residues to leach into groundwater when applied to cotton grown in sandy soils. Thus, to support this registration, an additional field dissipation study must be conducted where field dissipation and the leaching potential for amitraz and its soil degradates are investigated.

8.2 Inform the registrant that the submitted California field rotational crop study is acceptable and partially satisfies the data requirement for this study.

Only one representative cotton growing site--the arid southwestern U. S.--is represented. This is acceptable provided amitraz will not be registered for use in other cotton growing areas of the United States (i.e., the southeastern U. S.) or the label prohibits planting of rotational crops following cotton treated with amitraz in the other cotton growing areas of the United States. Otherwise, a field rotational crop study must be conducted in at a site representing the southeastern U. S.

8.3 Inform the registrant that the following studies still have deficiencies which must be resolved before the study can be accepted as satisfying the data requirement:

1. Photodegradation on Soil- The study was previously reviewed and was found acceptable. However, the registrant should provide the sensitivity of the detection method used in the study.

2. Leaching - Adsorption: EFGWB does not agree that the Freundlich K values are meaningless in this case. Therefore, the registrant should provide the Freundlich K values for the submitted adsorption study.

3. Fish Accumulation: The study may be acceptable if the location (in which fish tissue or whole body) of the reported degradates is supplied.

8.4 Inform the registrant that the requirement for the field volatility study is being reserved at this time.

In the Amitraz Registration Standard (Oct 1987), both lab and field volatility data were required for the use pattern (pears) in effect at that time. A laboratory volatility

study was reviewed by EFGWB in the EUP application for use on cotton and citrus, registration on citrus and response to the Registration Standard) and was found acceptable. The vapor pressure for amitraz (parent) was 2.6×10^{-6} mm Hg at 25° C which exceeded the criteria of concern ($>10^{-6}$ mm Hg) and triggered the requirement for a laboratory volatility study. In addition, the degradates of amitraz have vapor pressures ranging from 0.2 mm Hg to 2.6×10^{-5} mm Hg at 25° C.

8.5 Inform the registrant that the available environmental fate data support the proposed experimental use permit for use of amitraz on apples. While EFGWB has concerns about the potential for residues of amitraz to leach into groundwater from the proposed EUP, apple orchards are not usually planted in sandy soil as citrus orchards are.

The data considered for the EUP application indicate that:

1. Hydrolysis: Degradation occurred in the dark with half-lives of 2.1 hours at pH 5, 22.1 hours at pH 7, and 25.5 hours at pH 9. Major degradation products were BTS 27271 and BTS 27919. See Figure 1 for structures.

2. Aerobic soil degradation: Amitraz degraded in silt loam and sandy loam soils with a half-life of less than 1 day. Major degradation products were BTS 27271 and BTS 27919. Mineralization to CO_2 and soil binding appear to be the major means of dissipation in the soil environment.

3. Mobility-leaching and adsorption/desorption. Although EFGWB concludes that this study is still supplemental since adsorption coefficients (K_d) values were not calculated for the adsorption study, other data (soil TLC) indicate that amitraz residues were very mobile in sand and moderately mobile in sandy loam, silt loam and clay soils. Also, the soil column data indicate that the majority of residues were found in the upper 10 cm of soil columns. However, radioactivity was found in the leachate fractions. Other column studies judged supplemental indicated that aged residues may be more mobile in sand and loamy sand soil columns.

Note: All the numerous leaching studies reviewed so far have been judged supplemental. However, the available data suggest that residues of amitraz have the potential to leach to groundwater since the leaching data indicated moderate mobility in sandy loam, silt loam, and clay soils and rapid mobility in sandy soils.

Note: The field dissipation study indicated that the major metabolites may have a much longer half-life than the parent amitraz does.

4. Fish accumulation: Bluegill sunfish had maximum bioaccumulation factors of ca. 280X for muscle, 2118X for viscera, 1467 for carcass tissues and 933X for whole fish. After a 14 day depuration period, 86% to 89% of the accumulated residues were depurated. However, this study was judged deficient in that the location of the residues within the fish body was not identified.

5. Rotational crops: No data are required for this orchard use.

8.6 Inform the registrant that, for registration of these uses, the above data deficiencies must be resolved and data on the outstanding studies must be submitted and favorably reviewed. Additional field dissipation studies which determine the potential for amitraz residues to leach will be required to support the registration of amitraz for use on crops grown in sandy loam, silt loam, clay and sandy soils.

9. BACKGROUND:

NOR-AM Chemical is requesting the registration of this new product for use on cotton. A field rotational crop study was included with the registration request. A previous submission dealing with an EUP for use on cotton was reviewed by EFGWB in reviews dated June 28 and July 19, 1989.

NOR-AM is also requesting an experimental use permit for use of amitraz on apples. The experimental program proposes to use a total of 1,731 lbs. A.I. on a total of 525 acres of apple orchards.

10. DISCUSSION OF INDIVIDUAL STUDY:

See separate Data Evaluation Records (DERs) for the field rotational crop and aqueous photolysis studies.

11. COMPLETION OF ONE-LINER: The one-liner has been updated.

12. CBI APPENDIX: There is no CBI in this review.

DATA EVALUATION RECORD

STUDY IDENTIFICATION:

Castro, L. 1988. Residues of amitraz and its major metabolites in soil and rotational crops following application of MITAC EC to cotton; Lab Project #12010; NOR-AM Chemical Co.; Exton, PA. Accession #409995-09.

REVIEWED BY:

James Hetrick, Ph.D., Chemist Signature: James G. Hetrick
Environmental Chemistry Review Section 1 Date: 12/6/89

APPROVED BY:

Paul J. Mastradone, Ph.D., Chief Signature: Paul J Mastradone
Environmental Chemistry Review Section 1 Date:

TYPE OF STUDY: Field Rotational Crop

CONCLUSIONS:

1. EFGWB concludes that this California study is acceptable and partially satisfies this data requirement for the filed rotational crop study. The results of the study indicate that neither amitraz nor its metabolites were detected (>0.05 ppm) in the rotated crops red beets, cabbage, and wheat planted 44 or 113-155 days after the primary crop, cotton, was treated with amitraz at an application rate of 0.75 lb ai/A (single application) and 1.0 lb ai/A (treated twice at 0.5 lb ai/A each treatment).

2. However, EFGWB notes deficiencies in this study:

1. Only one geographical site is represented. This is acceptable provided amitraz will not be used in other cotton growing areas of the United States or the label prohibits planting of rotational crops following cotton treated with amitraz in the other cotton growing areas of the United States.

2. Soil was not sampled at times of planting of the rotational crops or at harvest of the rotational crops. However, since no residues were found in the soil one day after application, this deficiency does not effect EFGWB's conclusion.

3. Immature plant parts were not analyzed for those rotational crops which could be harvested or foraged at an immature stage (e.g., winter wheat).

4. The mature wheat samples were not separated into individual plant parts prior to analysis (i.e., into straw, chaff and grain).

5. Rotational crop samples were not analyzed for parent amitraz and the individual metabolites. However, because no residues were found in the rotational crops, this deficiency does not effect EFGWB's conclusion.

MATERIALS AND METHODS:

Cotton, the primary crop, was treated with amitraz (Mitac EC formulation, 19.8% ai) at (1) mid-season with 0.75 lb ai/A and (2) at early and mid-season with 0.5 lb ia/A each time. The test plots were at the NOR-AM field station in Fresno, CA in a sandy loam soil (See Table for soil characteristics). Two rotation plans were tested: one half of each plot was mowed and disced 30 days after the last treatment (to simulate early crop failure and rotation interval of 44 days) and planted two weeks later with rotated crops of red beets, cabbage, and winter wheat. The other half of the plot was planted to the same rotated crops after harvest of the mature cotton (to simulate a normal rotation interval of 113 or 153 days).

Soil was sampled at times "bracketing" the dates of (1) final application, (2) emergency replanting (44 days after treatment), (3) normal rotation (113 or 155 days after treatment), (4) harvest from emergency replanting and (5) harvest from normal rotation. [e.g., For date of emergency replanting (44 days after treatment) soil was sampled 16 days before the 44 days (or 18 days) after treatment and at 21 days after the 44th day (or 65 days) after treatment. See Table 4] Each soil sample was taken as three replicates and (for analysis) divided into 0-6 and 6-12 inch cores.

The rotated crops were harvested at maturity and stored frozen until analysis.

The analysis of the crops (chopped while frozen) involved acid and base hydrolysis, partitioning of the released amitraz fragment, 2,4-dimethylaniline (DMA), into hexane, then derivatization of DMA with heptafluorobutyric anhydride. Final analysis was by gas chromatography of the DMA derivative. The limit of detection of the method is 0.05 ppm. All residues were reported as amitraz equivalents (conversion factor = 1.2107).

Soil samples were analyzed for amitraz and metabolites BTS 27271 and BTS 27919 by methods specific for each compound and analyzed to a limit of detection of 0.05 ppm for each compound:

Amitraz was extracted from the soil with acetone, then soil was vacuum filtered. The acetone was evaporated, the amitraz residues were redissolved in ethyl acetate and toluene.

Quantitation of amitraz was by GC.

BTS 27271 was extracted with 1 N NaOH and toluene. The toluene was collected and the BTS 27271 was extracted into 0.2 N acetic acid. The acid was neutralized, BTS 27271 residues partitioned into toluene and analyzed by GC.

BTS 27919 was extracted from the soil with soxhlet extraction using toluene as the solvent. The toluene extraction was reduced in volume and analyzed by GC.

REPORTED RESULTS:

Analyses of fortified and unfortified crop samples gave the average recovery efficiency as 86%, with a range of 73 to 123%. Table 6

Analyses of fortified soil samples gave an average recovery efficiency of 92%, with a range of 78% to 120% (Table 7). No residues of amitraz or its metabolites were detected in rotated crops of beets, cabbage, or wheat planted either 44 days (emergency replant) or 113-155 (normal rotation) days following treatment with amitraz and harvested at maturity (Table 9)

Only soil sampled one day after treatment contained detectable residues of amitraz or its metabolites. In this sample, a total of 0.33 ppm residues were found in the 0-6 inch soil layer (from the 0.75 lb ai/A single application) and 0.05-0.06 ppm (from the 0.5 + 0.5 lb. ai/A two applications). Table 10.

DISCUSSION:

Based on the results of the study, EFGWB concludes that residues of amitraz will not occur in rotational crops planted in California when planted in soil where cotton had been previously treated with amitraz either at 0.75 lbs ai/A (single application) or 1.0 lb ai/A (split application).

However, EFGWB notes deficiencies in this study:

1. Only one geographical site is represented. This is acceptable provided amitraz will not be used in other cotton growing areas of the United States or the label prohibits planting of rotational crops following cotton treated with amitraz in the other cotton growing areas of the United States.

2. Soil was not sampled at times of planting of the rotational crops or at harvest of the rotational crops. However, since no residues were found in the soil one day after application, this deficiency does not effect EFGWB's conclusion.

3. Immature plant parts were not analyzed for those rotational crops which could be harvested or foraged at an immature stage (e.g., winter wheat or beets).

4. The mature wheat samples were not separated into individual plant parts prior to analysis (i.e., into straw, chaff and grain). However, because no detectable residues were found in the rotational crop, this deficiency does not effect EFGWB's conclusion.

5. Rotational crop samples were not analyzed for parent amitraz and the individual metabolites. However, because no residues were found in the rotational crops, this deficiency does not effect EFGWB's conclusion.

DATA EVALUATION RECORD

STUDY IDENTIFICATION:

Brehm, A. 1988. (W101 Addendum) The Photolysis of Amitraz (Shering Code No.ZK 49 974) In Aqueous Solution. Shering Agrochemicals Limited (UK) for NOR-AM Chemical Co. MRID No. 412067-03.

TYPE OF STUDY: Aqueous photolysis

REVIEWED BY:

James Hetrick, Ph.D., Chemist Signature: James G. Hetrick
Environmental Chemistry Review Section 1 Date: 12/6/84

APPROVED BY:

Paul J. Mastradone, Ph.D., Chief Signature: Paul J. Mastradone
Environmental Chemistry Review Section 1 Date: DEC - 6

CONCLUSIONS:

EFGWB concludes that the study is scientifically sound and supports the conclusions drawn from the laboratory study. EFGWB concludes that amitraz may photodegrade in the aqueous environment with a half-life of about 4 days. However, hydrolysis appears to contribute to the degradation of amitraz in the aquatic environment. Amitraz degraded with a half-life of about 16 hours in the dark control sample (as opposed to about 14 hours in the exposed sample).

MATERIALS AND METHODS:

^{14}C-UL-phenyl-amitraz (specific activity 5.0 MBq/mg, >98% radiochemical purity) was added to 0.1M phosphate buffer pH 7 solution containing 1% acetonitrile to a concentration of 0.04 ppm in a series of test tubes, placed on the roof in an unshaded location and exposed to natural sunlight in Berlin, Germany (latitude 52° 30'). A set of dark controls wrapped in aluminum foil was also maintained. Samples were taken after exposure times of 3.6, 7.8 and 27.6 hours. See Table III for meteorological conditions during the study.

Aliquots of samples taken at time 0 and at exposure intervals were analyzed by high performance liquid chromatography using a flow-through radioactivity detector

REPORTED RESULTS:

The exposed and dark control samples showed the same radioactive peaks identified as parent amitraz and its hydrolysis products

BTS 27919 and BTS 27271. After 27.6 hours test duration, 23.3% and 18.7% of the applied radioactivity remained as parent amitraz in the dark (control) sample and in the irradiated sample, respectively. The degradates BTS 27271 and BTS 27919 accounted for 31.3%-45.2% and for 31.7%-40.5% of the applied radioactivity in the irradiated and dark control samples, respectively.

Based on the results of the study, the author calculated a half-life of 16.6 hours in the dark solution (1st order rate constant 0.0417 h^{-1}) and of 14.2 hours (1st order rate constant 0.0490 h^{-1}) in the irradiated solution. The degradation of amitraz in the photolytic solution was due to photolysis as well as dark (hydrolytic) reactions. Therefore the corrected photolytic rate constant is 0.0073 h^{-1} and corresponding half-life is 4 days (95.0 hours).

Based on the results of this study, the author concluded that this study confirms the results reported in the artificial light (mercury-arc) study and that those results could be extrapolated to natural sunlight conditions.

DISCUSSION:

EFGWB concludes that the study is scientifically sound and supports the conclusions drawn from the laboratory study. The results of the study show that amitraz degraded with half-lives of 16 hours in the dark control solution and of 14 hours in the irradiated solution. Metabolites BTS 27919 and BTS 27271 were the major degradates found in both solutions..

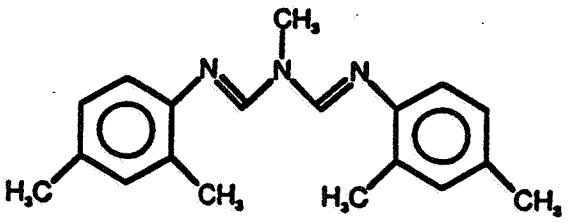
EFGWB concludes that amitraz may photodegrade in the aqueous environment with a half-life of about 4 days (via photolysis alone). However, the data suggest that hydrolysis appears to compete with photolysis for degradation of amitraz in the aquatic environment.

Note: The previous review indicated that the aqueous photolysis study was unacceptable since the test solutions were not sterilized. In addition, 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 adsorption spectra of amitraz in the test solutions were not provided. This study has some of the same deficiencies. However, EFGWB concludes that little additional information would be gained by requiring the registrant to repeat the study.

Appendix I

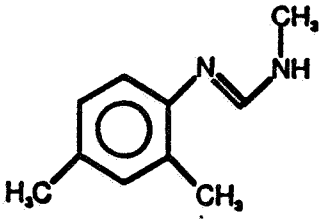
Molecular structures

Active ingredient

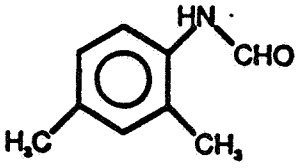


amitraz

Metabolites



BTS 27271



BTS 27919

B. Physical Properties

	Depth			
	0-7"	7-16"	16-44"	44-72"
Organic carbon - content(%)	0.44	0.22	0.10	0.06
Soil pH (in distilled H20)	6.4	6.5	6.7	6.8
Moisture held at 15 atmos(%)	2.8	2.6	2.0	2.0
% Sand	60.5	59.0	62.9	57.0
% Silt	32.0	34.0	32.0	39.0
% Clay	8.0	7.0	5.0	4.0
Cation exhange capacity (Meq. per 100 grams of soil)	12.0	15.0	18.3	17.3

Note: Information taken from T-M-T survey Table 1 "Profile description SE 40" and DWR Well Drillers Report.

Information taken from Independent survey by L. Stromberg.

Investigator [signature].....Witness: [signature].....Date: 05 04 82
Day Mo Yr

4.7.4 Calculations (continued)

The raw ppm was corrected for the average recovery efficiency of the method as experienced throughout sample analysis of this study (see Section 5.1). No correction was made for the apparent residues in the control samples. Soil results were also reported on a dry weight basis by multiplying the corrected ppm by (1 + GMC).

To calculate the total residue in soil as amitraz equivalents, it is necessary to correct for the stoichiometry of the degradation of amitraz: each molecule of BTS 27271 and BTS 27919 is the product of half a molecule of amitraz. Noting also that the molecular weight ratios of amitraz to BTS 27271 and BTS 27919 are 1.809 and 1.966, respectively, the total residue can then be calculated by equation 2.

total residue (ppm) = ppm amitraz + (1.809 x (ppm BTS 27271/2)) + (1.966 x (ppm BTS 27919/2)) (equation 2)

4.7.5 Representative chromatograms

Example chromatograms of calibration standards, control samples, fortified samples, and test samples may be found in Appendix III.

5 RESULTS AND DISCUSSION

5.1 Recovery efficiencies

Unfortified and fortified control samples of each matrix were analyzed alongside each set of treated samples. Most fortifications were performed at the limit of determination (0.05 ppm) as the levels of residues expected in this type of study are very low. Crops were fortified only with amitraz, but soil samples were fortified with amitraz, BTS 27271, or BTS 27919, depending on which analytical method was being used. Tables 6, 7, and 8 list the recovery efficiency from crops, the recovery efficiency from soil, and the apparent residues in the controls, respectively. Recoveries were calculated after subtraction of any apparent residues in the unfortified sample run in the same analysis set. The crop method has been fully validated for amitraz, BTS 27271, and BTS 27919 (5).

Table 6

Recovery efficiency from crops

Crop	Fortification level (ppm)	Fraction recovered (%)
Beet, red		
tops	0.05	75, 69
roots	0.05	84, 123
Cabbage	0.05	117, 68
Wheat	0.05	81
	0.1	73
Number		8
Average		86
Std. dev.		22

Table 7

Recovery efficiency from soil

Fortification level (ppm)	Fraction recovered (%) amitraz	BTS 27271	BTS 27919
0.04	NP (a)	68, 61, 78	NP
0.05	84, 86	NP	83, 85, 120, 87
0.08	NP	75, 79	NP
0.10	80	NP	94, 78, 98
0.16	NP	64	NP
Number	3	6	7
Average	83	71	92
Std. dev.	3	8	14

(a) NP = not performed at this level

Table 8

Apparent residues in control samples

Matrix	Sample description	Apparent residues (ppm) amitraz	BTS 27271	BTS 27919
Beet			NOTE: a total residue method was used for crop samples. This method analyzed for all three compounds simultaneously.	
top	emergency planting, rep. 1	0.002, 0.001		
roots	emergency planting, rep. 1	0.002, ND (a)		
Cabbage	normal planting, rep. 1	0.002, ND		
Wheat	emergency planting, rep. 1	ND		
	normal planting, rep. 1	ND		
Soil	3-month, rep. 3, 0-3"	NA (b)	ND, 0.013	NA
	4-month, rep. 3, 0-3"	ND, ND	0.006	NA
	6-month, rep. 2, 0-3"	ND	NA	ND, ND
	6-month, rep. 3, 0-3"	NA	ND, ND, ND	NA
	3-month, rep. 2, 3-6"	NA	NA	ND
	6-month, rep. 2, 3-6"	NA	NA	ND, ND, ND, ND

(a) ND = not detected.
(b) NA = not analyzed.

5.2 Limit of determination

Amitraz could be determined in crops samples to 0.05 ppm based on total residues. In soil, amitraz, BTS 27271, and BTS 27919 could be determined satisfactorily to 0.05 ppm on an individual compound basis.

5.3 Residues in treated samples

5.3.1 Rotational crops

No residues exceeding the limit of determination (0.05 ppm) were detected in any crop samples regardless of the treatment regimen used or the rotation timing. Table 9 lists the results obtained from the analysis of each treated sample.

Table 9

Residues in rotational crops

Matrix	Application rate (lb ai/A)	Planting scheme	Residues as amitraz (ppm) rep. 1	rep. 2	rep. 3
Beet tops	0.75	emergency	<0.05	<0.05	<0.05
		normal	<0.05	<0.05	<0.05
	0.5+0.5	emergency	<0.05	<0.05	<0.05
		normal	<0.05	<0.05	<0.05
Beet roots	0.75	emergency	<0.05	<0.05	<0.05
		normal	<0.05	<0.05	<0.05
	0.5+0.5	emergency	<0.05	<0.05	<0.05
		normal	<0.05	<0.05	<0.05
Cabbage	0.75	emergency	<0.05	NP (a)	NP
		normal	<0.05	<0.05	<0.05
	0.5+0.5	emergency	<0.05	NP	NP
		normal	<0.05	<0.05	<0.05
Wheat	0.75	emergency	<0.05	<0.05	<0.05
		normal	<0.05	<0.05	<0.05
	0.5+0.5	emergency	<0.05	<0.05	<0.05
		normal	<0.05	<0.05	<0.05

(a) NP = not performed.

Table 10
Residues in soil

Treatment rate (lb ai/A)	Relevant crops	Composite tested timepoint	Composite tested horizon	Corrected residues (ppm) amitraz	BTS 27271	BTS 27919	total (a)	GMC (%)
0.5 + 0.5	beets, wheat, & cabbage (all)	treatment	0-6" rep 1	<0.05	0.06	<0.05	0.05	21%
			0-6" rep 2	<0.05	0.05	<0.05	0.05	19%
			0-6" rep 3	<0.05	0.09	<0.05	0.08	20%
			6-12" rep 1	<0.05	<0.05	<0.05	---	20%
			6-12" rep 2	<0.05	<0.05	<0.05	---	21%
			6-12" rep 3	<0.05	<0.05	<0.05	---	18%
		1st planting: before	0-6"	<0.05	<0.05	<0.05	---	3%
			6-12"	<0.05	<0.05	<0.05	---	3%
		1st planting: after	0-6"	NA (b)	<0.05	<0.05	---	5%
			6-12"	NA	<0.05	<0.05	---	19%
	beets & cabbage	2nd planting: before	0-6"	NA	<0.05	<0.05	---	11%
			6-12"	NA	<0.05	<0.05	---	9%
		2nd planting: after	0-6"	NA	<0.05	<0.05	---	11%
			6-12"	NA	<0.05	<0.05	---	8%
	wheat	2nd planting	0-6"	NA	<0.05	<0.05	---	14%
			6-12"	NA	<0.05	<0.05	---	24%
	cabbage, wheat & beets	harvest: before	0-6"	NA	<0.05	<0.05	---	11%
			6-12"	NA	<0.05	<0.05	---	11%
		harvest: after	0-6"	NA	<0.05	<0.05	---	21%
			6-12"	NA	<0.05	<0.05	---	22%
0.75	beets, wheat, & cabbage	treatment	0-6" rep 1	<0.05	<0.05	<0.05	---	10%
			0-6" rep 2	0.07	0.18	0.10	0.33	20%
			0-6" rep 3	<0.05	<0.05	<0.05	---	7%
			6-12" rep 1	<0.05	<0.05	<0.05	---	11%
			6-12" rep 2	<0.05	<0.05	<0.05	---	8%
			6-12" rep 3	<0.05	<0.05	<0.05	---	9%
		1st planting: before	0-6"	<0.05	<0.05	<0.05	---	2%
			6-12"	<0.05	<0.05	<0.05	---	3%
		1st planting: after	0-6"	NA (a)	<0.05	<0.05	---	7%
			6-12"	NA	<0.05	<0.05	---	3%
	beets & cabbage	2nd planting: before	0-6"	NA	<0.05	<0.05	---	26%
			6-12"	NA	<0.05	<0.05	---	27%
		2nd planting: after	0-6"	NA	<0.05	<0.05	---	10%
			6-12"	NA	<0.05	<0.05	---	10%
	wheat	2nd planting	0-6"	NA	<0.05	<0.05	---	14%
			6-12"	NA	<0.05	<0.05	---	11%
	cabbage, wheat & beets	harvest: before	0-6"	NA	<0.05	<0.05	---	15%
			6-12"	NA	<0.05	<0.05	---	27%
		harvest: after	0-6"	NA	<0.05	<0.05	---	20%
			6-12"	NA	<0.05	<0.05	---	12%

(a) ---- indicates that no residues above the limit of determination were detected in this composite.
(b) This composite was not analyzed. An earlier timepoint did not contain detectable residues. No amitraz residues were expected in this sample.

Table I: Distribution of radioactivity in the HPLC-chromatograms from dark and photolysis solutions (values in % of total radioactivity in the HPLC-chromatograms)

	time [h]	radioactivity in peak 1 BTS 27919 [%]	2 BTS 27271 [%]	3 amitraz [%]
dark	0	11.0	7.6	76.8
	3.6	18.9	28.2	62.2
	7.8	27.9	22.1	45.8
	27.6	40.5	31.7	23.3
irradiated	0	11.0	7.6	76.8
	3.6	18.6	14.9	60.9
	7.8	34.8	23.2	35.8
	27.6	45.2	31.3	18.7

The times given in table I are the times between start of the sunlight irradiation and sampling. Handling times of the solutions before irradiation and times between sampling and analysis (max. 1 h) are not included (therefore some degradation products were already observed in the start solutions).

Nevertheless, these times could be used for an estimation of the degradation rates of amitraz in photolysis and dark solutions (using the amount of radioactivity corresponding to amitraz from table I) according the first order rate law:

$$\ln c = \ln c_o - k \cdot t$$

with c_o = amount of amitraz at t = o
k = first order rate constant

The results of the corresponding linear regression calculations (for details see appendix III) are given in table II.

Table II

	dark solution	photolysis solution
1st order rate constant [h^{-1}]	0.0417	0.0490
half-life [h]	16.6	14.2

Appendix II

Table III: Metereological conditions (Berlin-Dahlem, in 3 h intervals) during the experiment and sampling times with results of temperature measurements

date	time [h] MEZ*	temperature [°C]	sunshine** [h]	global irradiation*** [mWh/cm²]	sampling time [h] MEZ		temperature [°C] of dark solution	temperature [°C] of irradiated solution
15.06.88	1.00	12.6	-	-				
	4.00	11.5	-	0.2				
	7.00	15.0	1.6	23.1	start	6.52		
	10.00	19.0	2.1	62.4				
	13.00	21.7	3.0	87.8	sample 1	10.30	28.2	29.6
	16.00	23.0	3.0	66.9	sample 2	14.40	32.6	34.0
	19.00	21.0	1.4	11.6				
	22.00	18.1	-	-				
16.06.88	1.00	15.7	-	-				
	4.00	13.6	0.2	0.2				
	7.00	14.8	2.9	28.3				
	10.00	19.0	2.9	71.8				
	13.00	21.0	2.9	84.9	sample 3	10.30	31.0	33.0
	16.00	22.0	1.8	21.2				
	19.00	20.1	1.4	13.2				
	22.00	17.2	-	-				

sunrise 3.43 h, sunset 20.32 h (on both days)

global irradiation energies: 768.4 mWh/cm² 15.06.88
604.3 mWh/cm² 16.06.88 integrated values over full day

* MEZ = central European time ≙ local time -1 h (Summertime)

** time of sunshine in previous 3 h interval

*** integrated irradiation energy in the last hour of the 3 h interval ending at this time