Appendix B

Status of Fate Studies, Detailed Descriptions of Guideline Studies, and the Molecular Structures of Trifluralin and Its Degradates

Status of Fate Studies

Table B-1. Environmental Fate Data Requirements for Trifluralin				
Guideline #		**Data Requirement**	**MRID #'s**	**Data Requirement Status**
161-1	835.212	Hydrolysis	00131135	Supplemental
161-2	835.224	Photodegradation in Water	40560101	Supplemental
161-3	835.241	Photodegradation on Soil	40597801	Supplemental
162-1	835.41	Aerobic Soil Metabolism	41240501	Supplemental
162-2	835.42	Anaerobic Soil Metabolism	41240502	Supplemental
162-3	835.44	Anaerobic Aquatic Metabolism	Not Submitted	Not Submitted
162-4	835.43	Aerobic Aquatic Metabolism	Not Submitted	Not Submitted
163-1	835.1240 835.1230	Leaching-Adsorption/Desorption	40673501	Supplemental
163-2	835.141	Laboratory Volatility	40673601A 40673601B 40673601C	Supplemental Supplemental Supplemental
163-3	835.81	Field Volatility	40673601D 40673601E 40673601F 40673601G	Supplemental Supplemental Supplemental Supplemental
164-1	835.61	Terrestrial Field Dissipation	42309101 41661101	Supplemental Supplemental
165-4	850.173	Accumulation in Fish	40673801	Supplemental

Detailed Descriptions of Guideline Studies

(1) Degradation

Hydrolysis: The study is classified as supplemental at this time. The hydrolysis study (MRID 00131135) was found to be acceptable in 1984-1985. However, comparison of that study to a study of photodegradation in water (MRID 40560101) indicates a discrepancy. Trifluralin was reported to be substantially more stable in the hydrolysis study than for the dark controls in the study of photodegradation in water. In order to fully understand the degradation and dissipation of trifluralin, this discrepancy needs to be addressed.

Photodegradation in Water: The submitted study is classified as supplemental data for the following reasons:

- There is a discrepancy between the dark control half life (about 20 days) and the relative stability reported for the hydrolysis study.

- Trifluralin appears to volatilize in preliminary testing. For a complete environmental fate assessment, measurements are needed of the fractions of volatile and nonvolatile parent and degradates over the course of the test.

The study reports that trifluralin degraded with a half-life of 8.93 hours in a sterile pH 7 aqueous buffer solution when exposed to a light source. In the dark control, trifluralin degraded with a half-life of 485 hours (or about 20 days). The major degradates identified in the samples exposed to light (with maximum percent of applied) were:

TR-15, (47.4%) 2-ethyl-7-nitro-5-trifluoromethylbenzimidazole;
TR-6, (29.8%) 5-trifluoromethyl3-nitro-1,2-benzene diamine; and (9.6%) 2-ethyl-7-nitro-1-propyl-5-trifluoromethylbenzimidazole

The fraction of applied radioactivity recovered as volatile residue was about 55% for control samples and about 70% for light-exposed samples (MRID 40560101).

Photodegradation on Soil: The available study of photodegradation is classified as supplemental. In order to validate the analytical data, a confirmatory analysis (preferably MS) is needed in addition to comparison to the Rf of reference standards. There are guideline concerns [soil moisture and sieve size were not furnished and a discrepancy in the half-life for photodegradation on soil control samples (66 days) and for aerobic soil metabolism data (189 days)] in the study methodology, as well.

The study reports (MRID 40597801) that trifluralin degraded with a reported half-life of 41 days when exposed to a light source on sandy loam soil. The half-life of dark control samples of trifluralin was reported to be 66 days. Two degradates, 2,6-dinitro-N-propyl-4 - trifluoromethylbenzenamine, and 2-ethyl-7nitro-5-trifluoromethylbenzimidazole- 3-oxide, were identified in the light exposed samples at maximum concentrations of 6.0% and 7.1% of applied radioactivity in the soil extract, respectively. Unidentified residues made up a maximum of <9.6% of soil extract at 29.8-day following treatment. At 29.8 days following treatment, 11.2%

of the applied radioactivity was not extracted. Also, carbon dioxide was reported to reach 5.79% of applied radioactivity in the exposed samples and 0% for the dark control samples during the testing period.

Aerobic Soil Metabolism: The aerobic soil metabolism study (MRID 41240501) is classified as supplemental. A complete environmental fate assessment of the degradation of trifluralin under aerobic conditions cannot be made at this time for the following reason: degradates present in the organic extracts at up to 7.6% of the applied (0.119 ppm) and in the aqueous extracts at up to 6.9% of the applied (0.108 ppm) were not characterized.

Trifluralin degraded with registrant-calculated half-lives of 189, 201, and 116 days in sandy loam, clay loam, and loam soils, respectively, when incubated aerobically in the dark at 22 C for 364 days. Seven degradates were identified. With maximum percentages of applied radioactivity in the test samples, the seven degradates are:

1) α,α,α-trifluoro-2,6-dinitro-N-propyl-p-toluidine
2) α,α,α-trifluoro-5-nitro-4-propyl-toluene- 3,4-diamine
3) 2-ethyl-7-nitro-1-propyl-5-(trifluoromethyl)benzimidazole-3-oxide
4) 2-ethyl-7-nitro-1-propyl-5-(trifluoromethyl) benzimidazole
5) 2-ethyl-7-nitro-5-(trifluoromethyl)benzimidazole
6) α,α,α-trifluoro-2,6-dinitro-p-cresol
7) 2,2'azoxybis(, , -trifluoro-6-nitro-N-propyl-p- toluidine

These degradates were identified in test samples at maximum concentrations (% applied radioactivity) 2.8 to 4.6%, 1.5 to 2.1%, 0.1 to 0.3%, 0.5 to 1.0%, 2.1 to 2.6%, 0.1 to 2.7%, and 0.8 to 3.0%. During the testing period of about one year trifluralin parent declined to less than 25% of applied radioactivity in all soils. At the same time volatile and unextractable residues increased to 21.7% and about 45% of applied radioactivity.

Anaerobic Soil Metabolism: The anaerobic soil metabolism study is classified as supplemental data. A complete assessment of trifluralin degradation under anaerobic conditions cannot be made at this time because important degradates were not identified: Degradates were not characterized that were present in organic extracts at up to 6.1% of applied radioactivity (0.099 ppm) and in aqueous extracts at up to 12.1% of applied (0.182 ppm).

Based on the study available, trifluralin degraded with registrant-calculated half-lives of 25-59 days in sandy loam, loam, and clay loam soils incubated anaerobically in the dark at 22 C for 60 days following an aerobic incubation period of 30 days. The major degradates identified were:

1) TR-4 (13.2), α,α,α -trifluoro-5-nitro-N4,N4-dipropyl-toluene- 3,4-diamine (which reached a maximum concentration of 5.4% and 13.2% of the applied radioactivity in the sandy loam soil and clay loam soil, respectively, at Day 60 following flooding, and 11.6% in the loam soil at Day 30 following flooding);

2) 7-amino-2-ethyl-1-propyl-5-(trifluoromethyl) benzimidazole (which reached 7.3% in the sandy loam soil and 8.3% in the loam and clay loam soils at Day 60 following flooding);

3) α,α,α-trifluoro-N4,N4-dipropyltoluene-3,4,5-triamine (which reached 0.3% in the sandy loam soil, 4.1% in the loam soil, and 2.6% in the clay loam soil).

Four other degradates identified were:

1) α,α,α-trifluoro-2,6-dinitro-N-propyl-p-toluidine;
2) α,α,α -trifluoro-5-nitro-N4-propyl-toluene-3,4-diamine;
3) 2-ethyl-7-nitro-1- propyl-5-(trifluoromethyl) benzimidazole;
4) 2,2'-azoxybis (, , -trifluoro-6-nitro-N-propyl- p-toluidine)

each present at concentrations up to 2.1% of the initial radioactivity.

The following three degradates:

1) 2-ethyl-7-nitro-1-propyl-5-(trifluoromethyl);
2) benzimidazole-3-oxide;
3) 7-amino-2-ethyl-5-(trifluoromethyl)benzimidazole;

were each present at up to 1% of the initial radioactivity. Uncharacterized degradates in the organic extracts were at maximum concentrations of 6.1% (0.099 ppm) of the initial radioactivity in the sandy loam soil, 6.2% (0.093 ppm) in the loam soil, and 6.3% (0.090 ppm) in the clay loam soil. Uncharacterized degradates in the aqueous extracts were maximums of 6.4% (0.104 ppm) of applied radioactivity in the sandy loam soil, 12.1% (0.182 ppm) in the loam soil, and 9.6% (0.138 ppm) in the clay loam soil. An increase of unextractable trifluralin residues (9.4 to 60%) indicated that binding of residues to soil organic matter is the major route of anaerobic dissipation for trifluralin (MRID 41240502).

(2) Mobility

Leaching and Adsorption-Desorption: The mobility study is classified as supplemental. Degradates that were detected in the soil segments extracts and the leachate were not quantified and characterized, as needed to predict the leaching of trifluralin residues.

Unaged trifluralin appears not to be mobile in sandy loam, loam, and clay loam soils (Freundlich K_{ads}, values of 54.8-155.6). However, aged trifluralin residues appear to be slightly mobile in columns of sand and loam soils: About 90% of the applied radioactivity remained in the upper 6 cm; 0.65-2.57% leached from the column. The degradates identified were:

1) α,α,α-trifluoro-2,6-dinitro-N-propyl-toluidine (TR-2) (present at 3.01-3.05% of the extracted radioactivity);
2) 2-ethyl-7-nitro-1-propyl-5-(trifluoromethyl)-benzimidazole (present at 0.77-0.87% of extracted radioactivity);
3) 2,2'-azoxybis(, , -trifluoro-6-nitro-N-propyl-p- toluidine) (present at 0.38-0.40% of extracted radioactivity).

Degradates remaining at the TLC origin were 0.88 to 1.31% of the extracted radioactivity. Also, radioactivity in other TLC zones ranged from 0.01 to 0.54% of extracted radioactivity. Uncharacterized residues in the aqueous extract averaged 0.76% of the applied radioactivity with unextracted residues averaging 6.79% of the applied radioactivity. Volatile residues extracted from the charcoal trap averaged 3.40% of the applied radioactivity. The extracted radioactivity in the charcoal trap was identified as essentially all trifluralin with some TR-2, and residues remaining at the TLC origin (MRID 40673501).

Laboratory Volatility: Three laboratory volatility studies are classified as supplemental data. These data were taken from published articles and were not originally designed to satisfy Subdivision N data requirements. Therefore, it is difficult to draw conclusions needed for an environmental fate assessment. However, published laboratory and field volatility data submitted (MRID 40673601A-G) do indicate the following:

1) Volatility may be a major route of dissipation for trifluralin above the soil surface.
2) Trifluralin appears to volatilize (25 to 60% of applied in 11 days).
3) Data are needed to determine relative rate of dissipation due to volatility in relation to other routes of dissipation.

In the data submitted, the concentration of trifluralin in air and soil was not reported. Also, application rate and material balances could not be confirmed, and the concentration of trifluralin residues in the air could not be related to the concentration of trifluralin residues in the soil. Furthermore, the study was terminated before the pattern of decline of the test substance was established (MRID 40673601A, 40673601B, 40673601C).

Field Volatility: Four field volatility studies were submitted and provide supplemental data. They cannot be used to fulfill the data requirement.

These data were taken from published articles and were not originally designed to satisfy Subdivision N data requirements. Therefore, it is difficult to draw the conclusions needed for an environmental fate assessment. However, published volatility data submitted do indicate the following:

1) Volatility may be a major route of dissipation for trifluralin above the soil surface.
2) Trifluralin appears to volatilize: 25% to 60% of applied trifluralin volatilizes in 11 days).

In the data submitted the concentration of trifluralin in the soil immediately following treatment was not reported. Therefore, the application rate was not confirmed and the concentration of trifluralin in the air could not be related to the amount of trifluralin in the soil.

Furthermore, the study was terminated before the pattern of decline of the test substance was established (MRID 40673601D, 40673601E, 40673601F, 40673601G).

(3) Field Dissipation

Terrestrial Field Dissipation: The terrestrial field dissipation studies are classified as supplemental. However, they cannot be used to fulfill the data requirement because degradates identified in laboratory data were not analyzed for in field samples, and the degradation pathway of trifluralin in the field could not be determined from this study.

Granular trifluralin dissipated with a reported half-life of 49 days in the top 6 inches of soil when applied to loamy sand soil in California. Pretreatment sample analysis indicated there were low levels (0.07-0.16 ppm) of trifluralin present at depths less than 6 inches. Immediately following treatment, concentrations ranged from 1.30 to 6.30 ppm and from 1.80 to 5.00 ppm for applications 1 and 2, respectively. By days 14 and 42 following treatment the average recovery was 1.14 ppm (range of 0.88-1.30 ppm) and 0.74 ppm (range of 0.38-1.90), respectively. With the exception of one sample, trifluralin was not detected at depths greater than 6 inches (MRID 41781901).

Trifluralin (EC formulations) dissipated with reported half-lives of 149 days from California loam soil and 93 days from Alabama clay soil. Immediately following treatment, the recoveries on 8 samples ranged from 2.10 to 6.70 ppm and from 1.40 to 2.90 ppm at depths to 6 inches for the CA and AL sites, respectively. By termination of the study (Day 494 following treatment for CA site and day 482 following treatment for AL site) the recovery of applied material had declined to 0.22 and 0.04 ppm, respectively. Trifluralin did not appear to leach to below 6 inches depth. However, one sample at 24 to 30 inches depth did contain trifluralin at 0.06 ppm, 494 days following treatment at the California site (MRID 41661101).

Emulsifiable concentrate trifluralin formulations were reported to dissipate with a half-life ranging from 29 to 35 days when applied to coarse (sandy loam soil at Shellman, GA site) and fine (silty clay loam soil at Mansfield, IL site) soils, respectively. However, granular trifluralin formulation was reported to dissipate with a half-life ranging from 15-to 86 days when applied to sandy loam soil in Shellman, GA. These half-lives were calculated from nonlinear dissipation curves. Furthermore, since trifluralin was not discernible in soil segments below the top 6 inches of soil, trifluralin did not demonstrate any leaching potential.

Mean recoveries immediately following treatment for the emulsifiable concentrate at the Georgia and Illinois sites were 0.94 ppm (132% of applied) and 0.99 ppm (200% of applied) at depths less than 6 inches, respectively. For the granular formulation the mean recoveries immediate

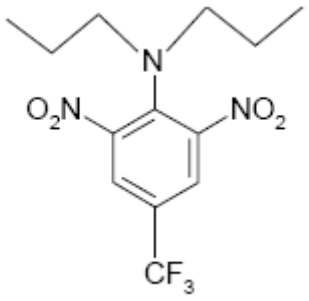
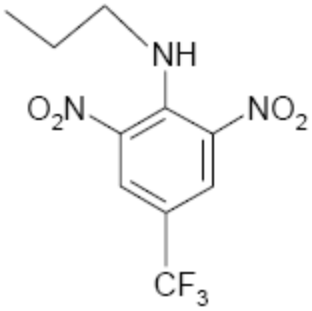
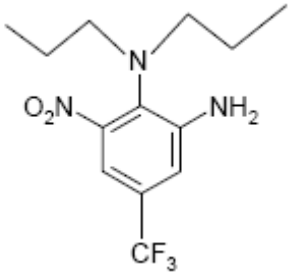
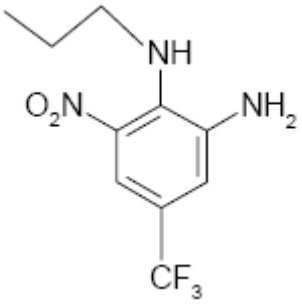
(4)Accumulation

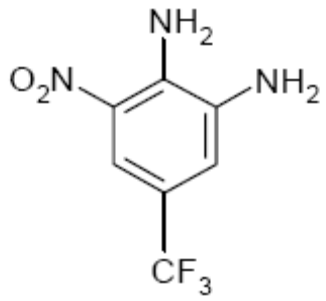
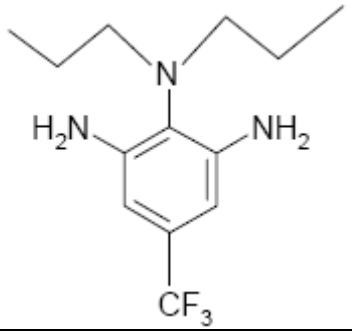
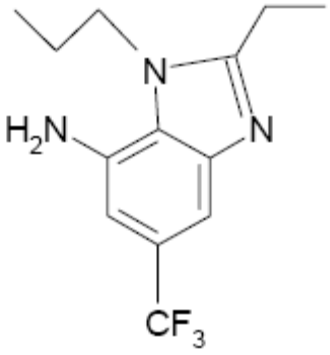
Bioaccumulation in Fish: The study submitted was classified as supplemental. Accumulation and depuration in fish cannot be fully assessed because radioactive residues in the fish tissues were not completely characterized. Radioactivity attributed to a total of 10 metabolites at a maximum of 0.804 ppm was not identified; up to 1.273 ppm was described only as polar radioactivity. Also, up to 1.8% of the total radioactivity in the aqueous phase of the tissue extracts was not characterized. Trifluralin residues accumulated in bluegill sunfish exposed to 0.0059 ppm of trifluralin, with maximum mean bioconcentration factors of 2041x, 9586x, and

5674x for edible, nonedible, and whole fish tissues, respectively. Depuration occurred with 86.34-88.01% of the [^{14}C]residues eliminated from the fish tissues after 14 days of exposure to pesticide free water (MRID 40673801).

following treatment at the Georgia and Illinois sites were 0.85 ppm (113% of applied) and 0.67 ppm (134% of applied), respectively. By termination of study, the mean recoveries for the emulsifiable concentrate were 0.04 ppm at 398 following treatment at the Illinois site and 0.09 ppm at Day 193 following treatment at the Georgia sites. For the granular formulation, at termination of study the mean recoveries were 0.04 ppm (Day 573 posttreatment) and 0.10 ppm (Day 549 posttreatment) for the Illinois and Georgia sites, respectively. There was an increase in the mean at Day 7 posttreatment at the Georgia site for the emulsifiable concentrate formulation (1.91 ppm which is 400% of applied) and at the Illinois site for the granular formulation (1.01 ppm which is 135% of applied)(MRID 42309101).

The Molecular Structures of Trifluralin and Its Degradates

Table A.1 Identification of Compounds in Plant and Animal Metabolism Study		
Common Name/Code	**Chemical Name**	**Chemical Structure**
Trifluralin	α,α,α-trifluoro-2,6-dinitro-*N*,*N*-dipropyl-*p*-toluidine	
TR-2	α,α,α-trifluoro-2,6-dinitro-Npropyl-p-toluidine 2,6-dinitro-Npropyl-4-triflurомethylbenzenamine	
TR-4	α,α,α-trifluoro-5-nitro-N4,N4-dipropyl-toluene-3,4-diamine	
TR-5	α,α,α-trifluoro-5-nitro-propyltoluene-3,4-diamine	

TR-6	5-trifluoromethyl-3-nitro-1,2-benzenediamine	
TR-7	α,α,α -trifluoro-N4,N4-dipropyltoluene-3,4,5-triamine	
TR-14	7-amino-2-ethyl-1-propyl-5-(trifluoromethyl) benzimidazole	
TR-15	2-ethyl-7-nitro-5-trifluromethylbenzimidazole