Shaughnessy No.: 128821

Date Out of EAB: SEP 25 1987

To: Robert Taylor
Product Manager 25
Registration Division (TS-767)

From: Therese Dougherty, Chief
Review Section #1
Exposure Assessment Branch
Hazard Evaluation Division (TS-769)

Attached, please find the EAB review of...

Reg./File # : 241-EOO

Chemical Name: Imazapyr

Type Product : Herbicide

Product Name : Arsenal

Company Name : American Cyanamid

Purpose : Registration for Forestry (New Use)

Action Code(s): 171

EAB #(s) : 70765

Date Received: 6/19/87

TAIS Code:

Date Completed: SEP 25 1987

Total Reviewing Time: 1 day

Deferrals to:

_____ Ecological Effects Branch

_____ Residue Chemistry Branch

_____ Toxicology Branch

Monitoring study requested by EAB: _____

Monitoring study voluntarily conducted by registrant: _____

1. CHEMICAL: Common name:

Imazapyr

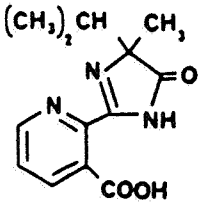
Chemical name:

2-(4-Isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-nicotinic acid

Trade name(s):

Arsenal, CL 252 925, AC 252 925

Structure:



Formulations:

200-250 g a.e. imazapyr-isopropylammonium/L SC/L

Physical/Chemical properties:

Molecular formula: $C_{16}H_{15}N_3O_3$
Molecular weight: 261.3.
Physical state: Colorless solid.
Melting point: 128-130°C.
Solubility: In water - 620-650 g/L at 25°C.
Octanol/water partition coefficient: 1.3 at 22°C.

2. TEST MATERIAL:

Arsenal

3. STUDY/ACTION TYPE:

Application for registration on forestry use sites.

4. STUDY IDENTIFICATION:

The following study was reviewed as a new submittal:

Michael, J.L. and W.D. Boyer. 1986. Fate of Arsenal in forest watersheds after aerial application for forest weed control. FS-80-4105-1.20. Prepared by U.S. Forest Service, Auburn, AL, and submitted by American Cyanamid Company, Princeton, NJ. (MRID 40003714)

5. REVIEWED BY:

Stephen J. Simko
Chemist
EAB/HED/OPP

Signature: S. Simko 9/25/87

6. APPROVED BY:

T. Dougherty
Chief, Section 1
EAB/HED/OPP

Signature: Theresa M. Dougherty SEP 25 1987

7. CONCLUSIONS:

Imazapyr was applied at 2.24 kg ai/ha to forrest sites in Alabama. Imazapyr dissipated in the litter and soil by 90% within 45 days after the maximum concentration was measured. Foliage residues fell from a maximum of 123 ppb to a 12 ppb by 14 days posttreatment. The Half-life of imazapyr ranged from 37 to 44 days in litter, 19 to 34 days in soil, and 12 to 40 days in plants. Stream water that was sprayed had an average of 169 ppb for the day of treatment. Only one sediment sample was positive (50-52 ppb, one month post-treatment).

Runoff appears to be a significant factor in the contamination of streams. Following the first rain event at the Fayette site, the stream concentration of imazapyr was 488 ppb and dropped back to background levels within 40 days. Residues were detected in 1% of the samples below 30 cm (12 in.), with 3 positives in the 30-40 cm layer and 3 in the 40-50 cm layer. The depth of leaching of imazapyr will be assessed in the field dissipation study requested.

8. RECOMMENDATIONS:

The forrestry study submitted for this review was satisfactory. The results of the weed and soil study previously reviewed demonstrate that parent imazapyr is the major soil residue and is an adequate marker for this forrestry study.

A meeting was held with the registrant on 7/24/87. One issue raised by the registrant was that the forrest use of imazapyr requires only one or two applications over a 25 year period. However, EAB will still impose the full forestry data requirements for this infrequent use. Another issue was the analytical method for the anaerobic aquatic metabolism and photodegradation study reviewed by EAB on 6/23/87. Based on the identification of residues previously determined in the weed and soil metabolism study, the results from the anaerobic aquatic and soil photodegradation studies are sufficient and those data gaps are fulfilled.

Data Requirements Satisfied

-Hydrolysis
-Soil photolysis

-Aqueous photolysis
-Aqueous anaerobic metabolism
-Mobility
-Fish accumulation

Additional Data Gaps

-Aerobic soil metabolism - a study using ^{14}C-labeling in another portion of the molecule is needed to better define and identify degradation products.

-Field dissipation - another study is needed giving adequate sampling at sufficient depth to define the extent of leaching. The depth of leaching should be defined and samples should be analyzed for 2 feet below the level where residues are detected. The level of sensitivity for soil residues should be about 10 ppb. The maximum recommended application rate must be used. In addition to the parent compound, major degradates found in the aerobic soil metabolism study + CL 252,974 should be measured.

9. BACKGROUND:

This study was submitted in support of registration of imazapyr for forestry use. Directions specify foliar application at a maximum rate of 3 pints per acre (Arsenal contains 4 lbs ai/gal).

10. DISCUSSION OF INDIVIDUAL TESTS OR STUDIES:

See attached review.

11. COMPLETION OF ONE-LINER: N/A

12. CBI APPENDIX: No CBI is included.

CASE GS -- IMAZAPYR STUDY 1 PM --

CHEM 128821 Imazapyr

BRANCH EAB DISC --

FORMULATION 15 - SQLUBLE CONCENTRATE (SC/L)

FICHE/MASTER ID 40003714 CONTENT CAT 01

Michael, J.L. and W.D. Boyer. 1986. Fate of Arsenal in forest watersheds after aerial application for forest weed control. FS-80-4105-1.20. Prepared by U.S. Forest Service, Auburn, AL, and submitted by American Cyanamid Company, Princeton, NJ.

SUBST. CLASS = S.

DIRECT RVW TIME = 15 (MH) START-DATE END DATE

REVIEWED BY: K. Patten
TITLE: Staff Scientist
ORG: Dynamac Corp., Rockville, MD
TEL: 468-2500

APPROVED BY: S. Simko
TITLE: Chemist
ORG: EAB/HED/OPP
TEL: 557-0237

SIGNATURE: S. Simko 9/25/87 DATE:

CONCLUSIONS:

Field Dissipation - Forestry

1. This study is scientifically sound and provides supplemental information towards the registration of imazapyr.

2. Imazapyr (Arsenal, test substance not further characterized), at 2.24 kg ai/ha, dissipated with a half-life of <14 days in the tree foliage from mature and immature forested sites in Alabama in May-June, 1985. Maximum concentrations in the foliage were 100-123 ppb and decreased to 8-12 ppb by 14 days posttreatment. The maximum concentration of imazapyr in the litter layer, soil under litter, and bare soil was lower at the mature site, which had a dense overstory, than at the immature site, which contained primarily seedlings. At the mature site, maximum concentrations of imazapyr were 58 ppm in the litter layer, 1.6 ppm in soil under litter, and 1.6 ppm in bare soil. At the immature site, maximum concentrations of imazapyr were 185 ppm in the litter layer, 2.6 ppm in soil under litter, and 3.0 ppm in bare soil. At both sites, imazapyr in the litter and soil dissipated by 90% within 45 days after the maximum concentration. Imazapyr was detected as deep

as 40-50 cm in the soil (mature site, bare soil, day 28). The maximum concentration of imazapyr in the stream water was much greater at the mature site (169 ppb) where the stream was sprayed, than at the immature site (30 ppb) where a 15-foot buffer zone was left untreated on each side of the stream. Sediment samples contained <50-52 ppb of imazapyr (detection limit 50 ppb). Imazapyr in the streams was not diluted at distances up to 150 m from the treatment area.

3. This study fulfills EPA Data Requirements for Registering Pesticides.

MATERIALS AND METHODS:

Imazapyr (Arsenal, later mixed in 25% Igepal DM-70 surfactant, American Cyanamid Company) was applied at 2.24 kg ai/ha by helicopter in May-June, 1985, to two forested sites in Alabama (Table 1). Each site consisted of two adjacent but separate watersheds; one watershed was treated, the second served as the control. All sites were drained by permanent streams that were equipped with water level recorders, velocity recorders, and automatic water samplers. During pesticide application, a 15-m wide zone on both sides of the Wedowee stream was left untreated as a buffer zone. However, no attempt was made to avoid spraying the Fayette stream because the dense overstory made ground visibility from the helicopter poor.

Each watershed was divided into ridge, midslope, and lower slope subplots for the purpose of sampling. Hardwood foliage (overstory and understory were combined) was collected randomly from each subplot at intervals up to 360 days posttreatment; at the Wedowee site, foliage from the pine seedlings was also collected. Hardwood and pine foliage were frozen at -5°C until analysis. Samples (three 1-ft^2 samples per subplot) were collected from the litter layer and from exposed and litter-covered soil (0- to 10-, 10- to 20-, 20- to 30-, 30- to 40-, and 40- to 50-cm depths) using PVC pipe. The samples were frozen (-5°C) in the pipes until analysis. Water samples (1-L volume) were taken from within the treated areas, at the perimeter of the treated areas, and 30, 60, and 150 m below the perimeter. Sediment was filtered from the water. Sediment and water were frozen (-5°C) until analysis.

Vegetation samples (foliage and litter) were homogenized in a blender with dry ice. Subsamples were extracted with pH 6.5 phosphate buffer by shaking for 2 hours. The extract was filtered, mixed with methanol, and partitioned with methylene chloride. The methylene chloride phase was discarded, and the methanol phase was adjusted to pH 3 with 1 N hydrochloric acid and mixed with sodium chloride. The acidified methanol extract was partitioned three times with methylene chloride. The methylene chloride phases were combined, evaporated to dryness, and the residues were dissolved in acetone. The acetone solution was filtered through a Millex SR disposable filter. The eluate was evaporated to dryness and the residues were dissolved in methanol. The methanol solution was filtered through octyl and aromatic sulfonic acid Baker-10 SPE cartridges. The octyl cartridge was discarded, and imazapyr was eluted from the aromatic sulfonic acid cartridge with a pH 6.5 solution of di-

basic potassium phosphate in hydrochloric acid. The eluate was analyzed by HPLC with UV detection. Recovery efficiencies from six vegetation samples fortified at 0.05 and 20 ppm ranged from 83 to 117%. The detection limit was 0.05 ppm.

Soil and sediment samples were mixed thoroughly while partially frozen, then extracted with 0.5 N hydrochloric acid in methanol:water (1:1) by shaking for 30 minutes. The samples were vacuum-filtered, and the extract was adjusted to pH 2 with a 25% sodium hydroxide solution. The extract was partitioned four times with methylene chloride. The methylene chloride extracts were combined and mixed with a pH 7 monobasic potassium phosphate:sodium phosphate solution. The resulting methylene chloride phase was discarded, and the phosphate solution was adjusted to pH 2 with 1 N hydrochloric acid. The resulting solution was partitioned three times with methylene chloride. The methylene chloride extracts were combined, then dried and redissolved in methanol three times. The final methanol solution was mixed with 0.2 M trimethylanilinium hydroxide and immediately analyzed by GC with N-P detection. Recovery efficiencies from fortified samples ranged from 72.0 to 109.4%. The detection limit was 0.05 ppm.

Water samples were acidified to pH 2 with concentrated sulfuric acid. The acidified samples were filtered through C18 columns, and imazapyr was eluted from the columns with methanol. The methanol elutates were concentrated, diluted with 0.1 M phosphoric acid:methanol (80:20, v:v), and allowed to stand overnight. Samples were analyzed by HPLC with variable UV adsorbance detection. Recovery from fortified samples averaged 93.8 ± 10.6%. The detection limit was 1 ppb.

In order to establish the freezer stability of imazapyr, imazapyr was added at 197 ppb to plants, 500 ppb to soil, and 100 ppb to water. The treated samples were frozen (temperature not specified) for up to 22 weeks. Samples were analyzed for imazapyr as previously described.

REPORTED RESULTS:

Imazapyr dissipated with a half-life of <14 days in the tree foliage at the Fayette and Wedowee sites; the maximum concentrations were 100-123 ppb and decreased to 8-12 ppb by 14 days posttreatment (Figures 1 and 2). The maximum concentration of imazapyr in the litter layer, soil under litter, and bare soil was lower at the Fayette site, which had a dense overstory, than at the Wedowee site, which contained primarily seedlings (Figures 3, 4, and 5). At the Fayette site, maximum concentrations of imazapyr were 58 ppm in the litter layer, 1.6 ppm in soil under litter, and 1.6 ppm in bare soil. At the Wedowee site, maximum concentrations of imazapyr were 185 ppm in the litter layer, 2.6 ppm in soil under litter, and 3.0 ppm in bare soil. At both sites, imazapyr in the litter and soil dissipated by 90% within 45 days after the maximum concentration. Imazapyr was detected as deep as 40-50 cm in the soil (Fayette site, bare soil, day 28). The maximum concentration of imazapyr in the stream water was much greater at the Fayette site (169 ppb) where the stream was sprayed, than at the Wedowee site (30 ppb) where a 15-foot buffer zone was left untreated on each side of the stream (Figure 6). Sediment

samples contained <50-52 ppb of imazapyr (detection limit 50 ppb). Imazapyr in the streams was not diluted at distances up to 150 m from the treatment area.

Imazapyr did not degrade in plant, soil, and water samples stored frozen for 22 weeks.

DISCUSSION:

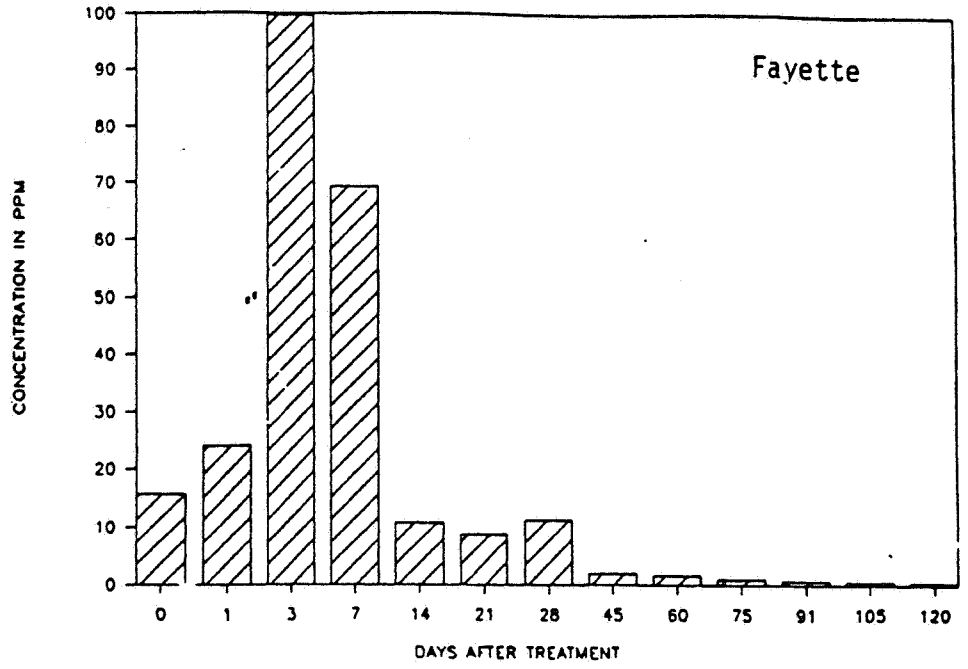
1. The pattern of formation and decline of degradates was not addressed. Samples were analyzed only for imazapyr.

2. The test substance was characterized only as Arsenal.

3. Tree foliage was not separated into upper canopy, midcanopy, lower canopy, and understory samples.

4. No samples of standing water were analyzed.

5. Air and soil temperatures were not reported. Precipitation data are presented in Figure 6.



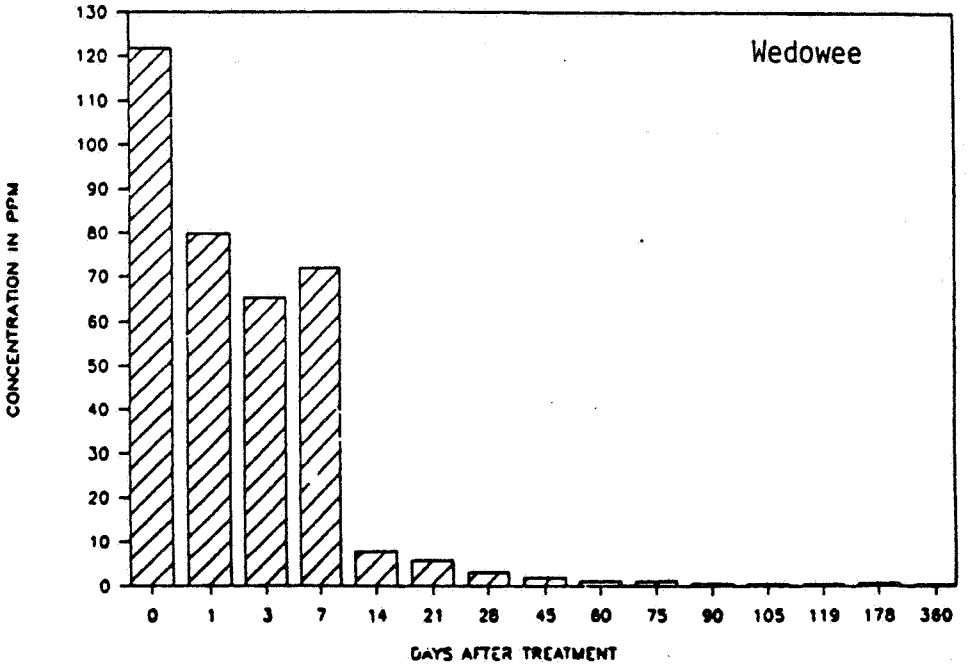


Figure 1. Imazapyr (ppm) in hardwood foliage from the Fayette and Wedowee sites following treatment of the forested sites with imazapyr (Arsenal, test substance not further characterized) at 2.24 kg ai/ha in May-June, 1985.

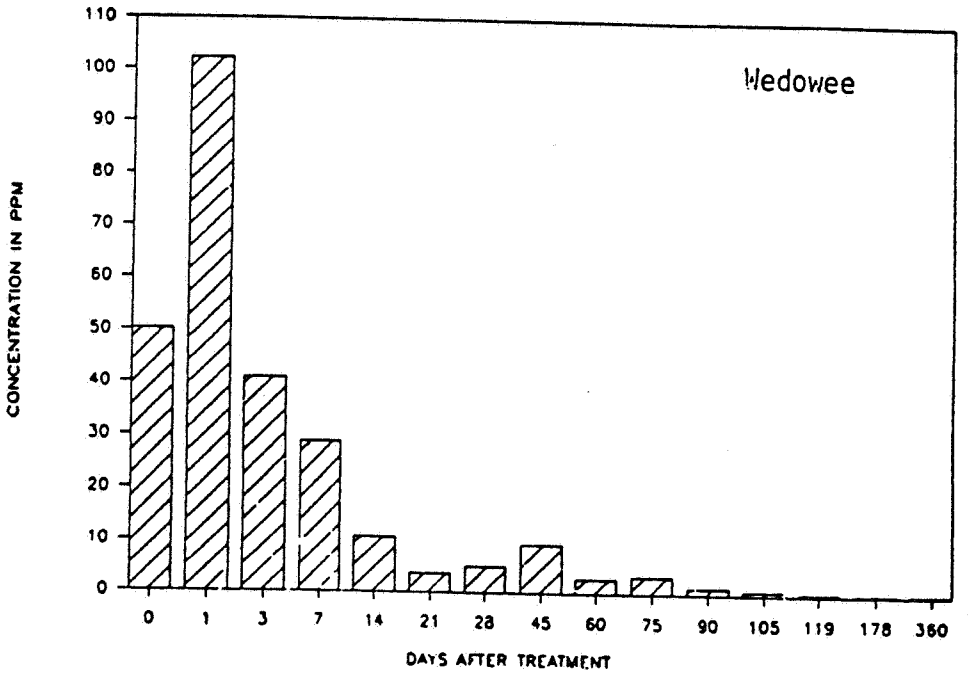


Figure 2. Imazapyr (ppm) in loblolly pine foliage from the Wedowee site following treatment of the forested site with imazapyr (Arsenal, test substance not further characterized) at 2.24 kg ai/ha in May-June, 1985.

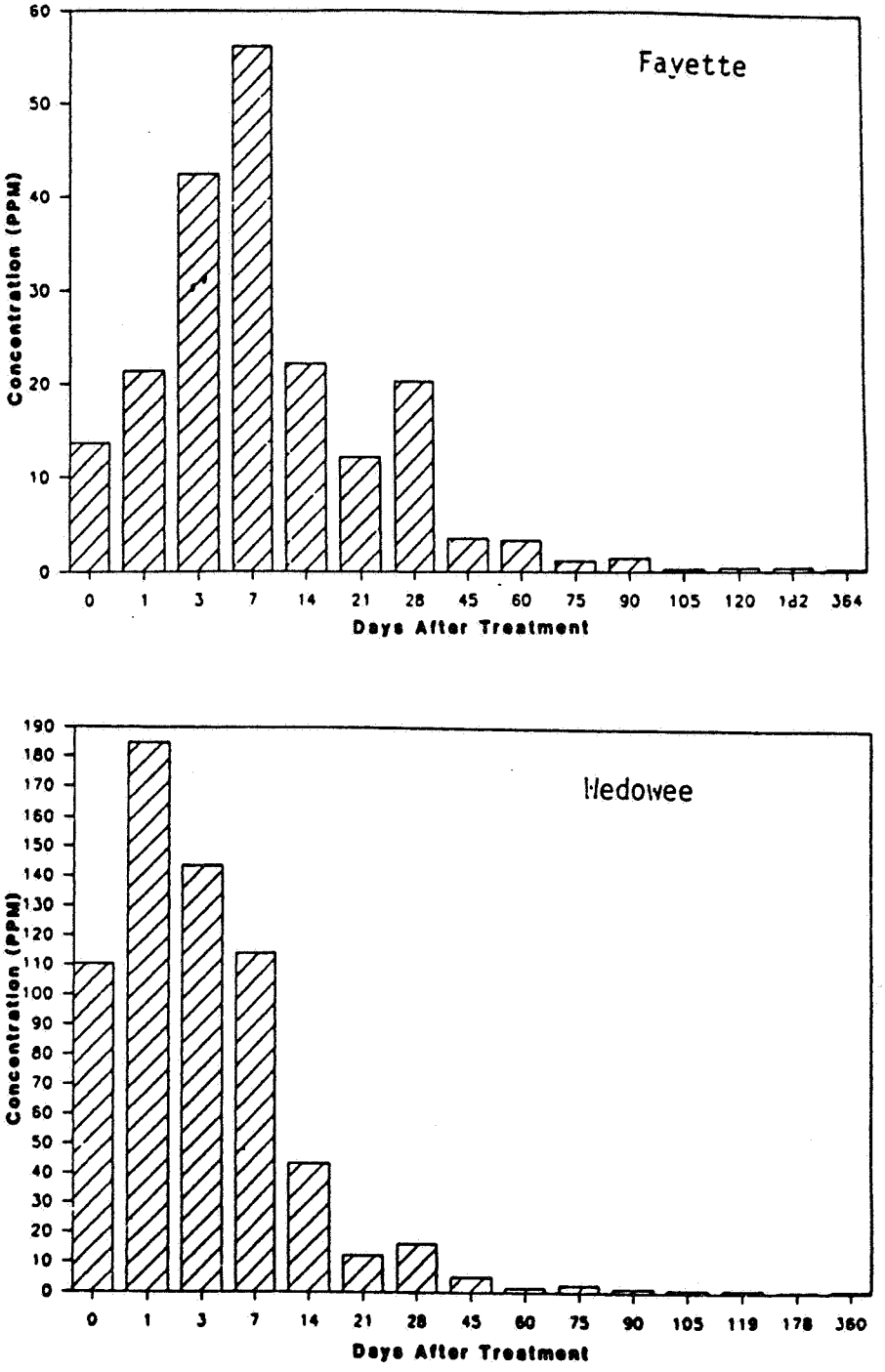


Figure 3. Imazapyr (ppm) in litter from the Fayette and Wedowee sites following treatment of the forested sites with imazapyr (Arsenal, test substance not further characterized) at 2.24 kg ai/ha in May-June, 1985.

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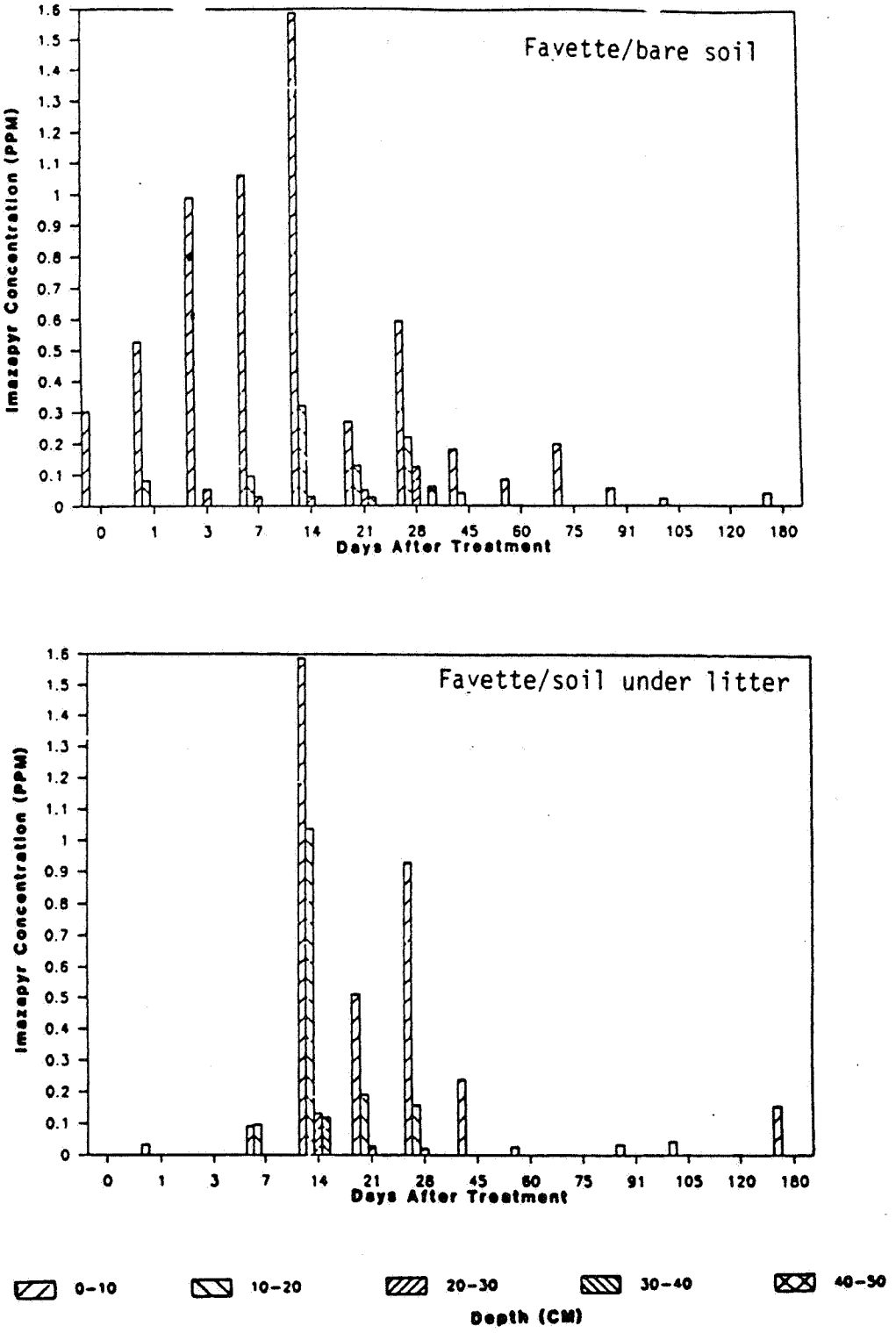


Figure 4. Imazapyr (ppm) in bare soil and soil under litter at the Fayette site following treatment of the forested site with imazapyr (Arsenal, test substance not further characterized) at 2.24 kg ai/ha in May-June, 1985.

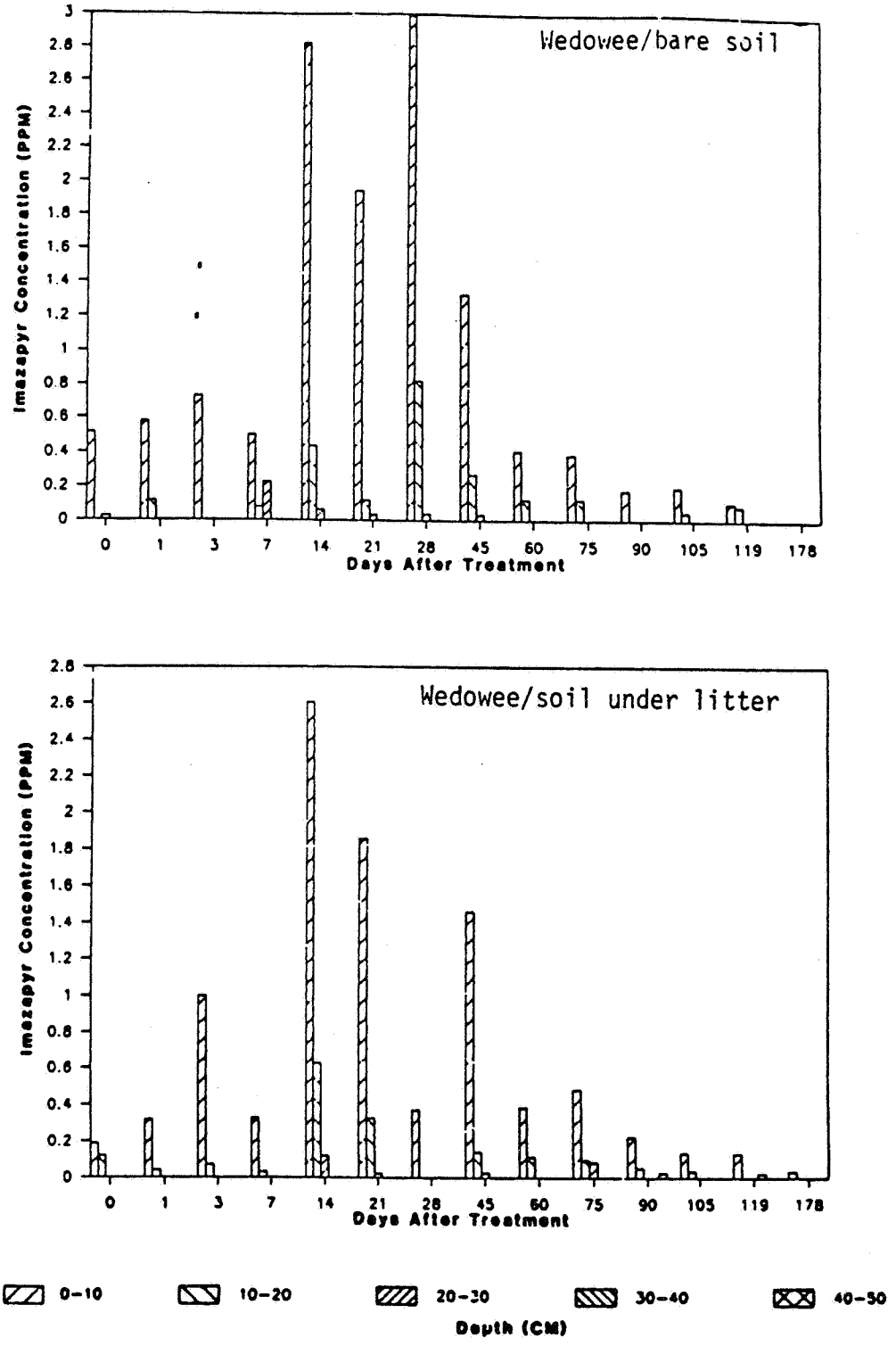


Figure 5. Imazapyr (ppm) in bare soil and soil under litter at the Wedowee site following treatment of the forested site with imazapyr (Arsenal, test substance not further characterized) at 2.24 kg ai/ha in May-June, 1985.

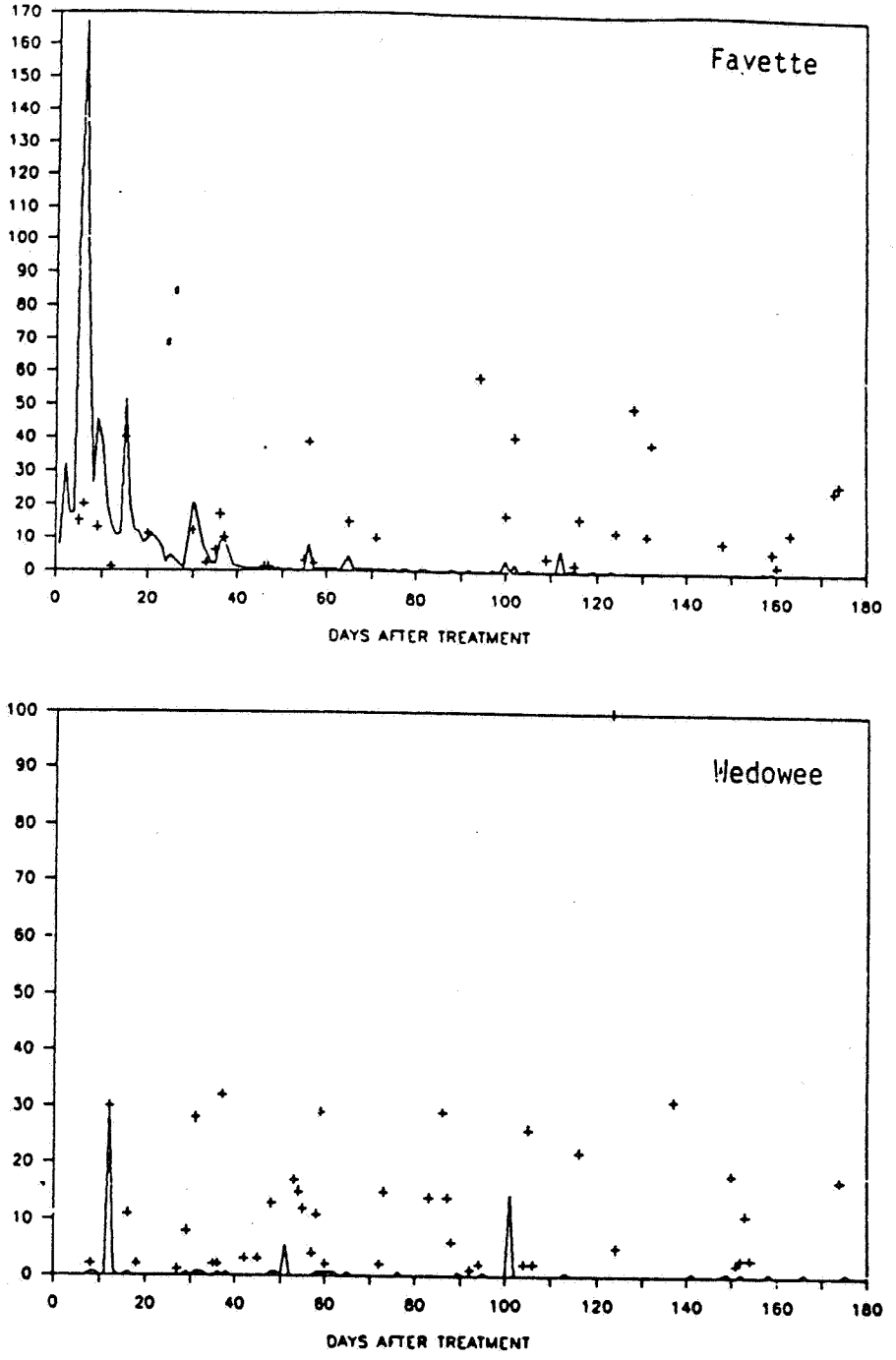


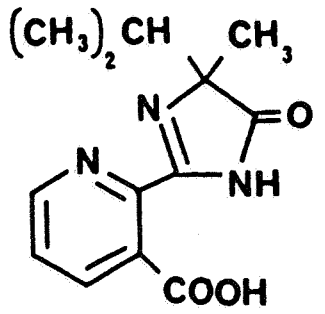
Figure 6. Imazapyr (ppb) in the Fayette and Wedowee streams following treatment of the forested sites with imazapyr (Arsenal, test substance not further characterized) at 2.24 kg ai/ha in May-June, 1985.

Table 1. Field test data.

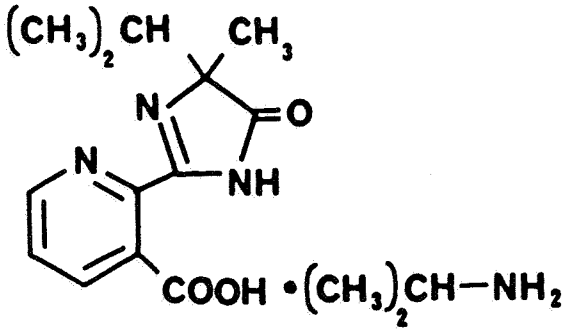
Parameter	Wedowee site	Fayette site
Location	East-central Alabama	North-western Alabama
Treatment date	5/30/85	6/18-21/86
Conditions at treatment	Near ideal	Fog, rain, winds < 5 km/hour
Soil type	Loam	Sandy loam
Sand	43.1	69.0
Silt	41.0	17.3
Clay	15.9	13.7
Organic matter	4.4	1.9
CEC	4.2	3.7
Vegetation	Immature loblolly pine (seedlings); blackjack oak	Dense mature hardwood overstory; mixed species
Plot size	87 hectares	40 hectares

Regression analysis of imazapyr dissipation and calculated half-life values for plant, soil, and litter.

Site	Matrix	Slope	Y-Intercept	P>F	R	Half-life (Days)
Fayette	Vegetation	-0.0232	1.537	0.0001	0.91	12
	Soil					
	Bareground	-0.0123	2.768	0.0001	0.77	24
	Under Litter	-0.0158	2.897	0.0001	0.84	19
	Litter	-0.0068	0.873	0.0001	0.73	44
Wedowee	Vegetation	-0.0086	0.965	0.0001	0.73	35
	Pine	-0.0076	0.947	0.0001	0.71	40
	Soil					
	Bareground	-0.0117	3.335	0.0001	0.89	26
	Under Litter	-0.0088	3.072	0.0001	0.80	34
	Litter	-0.0081	1.318	0.0001	0.74	37



2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)
nicotinic acid



2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)
nicotinic acid with isopropylamine (1:1)