(AUG 28 2003)

DATA EVALUATION RECORD

STUDY

CHEM 128821	Imazapyr	§164-2 and §165-5

CAS No. 81334-34-1
FORMULATION–AQUEOUS SOLUTION

STUDY ID 45119707
Borysewicz, R. F. 1999. Residues of CL 243997, CL 9140, and CL 119060 in aquatic field dissipation and aquatic non-target organisms for Arsenal® herbicide applied to freshwater ponds. Laboratory Project Identification: RES 99-059 and 99-060. Unpublished study performed by American Cyanamid Company, Princeton, NJ; Florida Pesticide Research, Oviedo, FL (in-life phase); Waterbourne Environmental, Inc., Columbia, MO (in-life phase); Centre Analytical Labs, Inc., State College, PA (analytical phase); and Maxim Technologies, Inc., Middleport, NY (analytical phase); and submitted by American Cyanamid Company, Princeton, NJ.

DIRECT REVIEW TIME =

REVIEWED BY: Dan Hunt SIGNATURE:
TITLE: Staff Scientist DATE:

EDITED BY: Joan Harlin SIGNATURE:
TITLE: Senior Staff Scientist DATE:

ORG: Dynamac Corporation
Rockville, MD
TEL: 301-417-9800

SECONDARY REVIEW AND
FINAL APPROVAL BY: Alex Clem SIGNATURE: Alex Clem
EPA DATE: 28 August 2003

2008399

ADMINISTRATIVE CONCLUSIONS

This study (MRID 45119707) for imazapyr (designated throughout the submission as CL 243997), is **unacceptable** for the purpose of **aquatic field dissipation (§164-2)**, and **supplemental** for the purpose of **bioconcentration in aquatic non-target organisms (fish and crayfish) (§165-5)**. However, within current EFED risk assessment methodologies, including use of reasonable and conservative default assumptions for modeling purposes, there would be little value added to the EFED risk assessment by the submission of additional study data. The registrant may, however, choose to submit new study data if they think results would significantly alter the overall EFED risk assessment. The registrant should carefully consider the critical elements cited in various sections of this Data Evaluation Record (DER), as these would generally prohibit the acceptability of future study submissions and elicit requirements for new studies. (For the record, portions of the study were not conducted according to Good Laboratory Practice (GLP), as attested on pages 7 and 328 of the submission, but, compared to other study limitations, the GLP exceptions are relatively unimportant.)

SCIENTIFIC CONCLUSIONS (in case of inadvertent differences, this section has precedence over subsequent sections of this report)

This aquatic field dissipation study for imazapyr did not account for the apparent relatively rapid disappearance of imazapyr (CL 243997) from the small (approximately 1/4 acre), shallow (approximately 2-3 feet deep) experimental ponds in Florida and Missouri (two ponds treated at each site). Pond water columns were analyzed for parent and for two degradates, CL 119060 and CL 9140, that were previously observed in major concentrations during laboratory aqueous photolysis. Neither of the photodegradates were observed in three of the four pond waters, and only minor concentrations of each were found in the remaining pond (see next paragraph). Pond sediment/soil was analyzed for parent only. No major routes of dissipation were identified in any pond.

Neither of the two photodegradates were found in the two Missouri pond waters, and only minor, sporadic concentrations of these were found in one of the two Florida pond waters. In the single pond where CL 119060 and CL 9140 were detected, the maximum concentration of each was approximately 5-6 ppb, which is only approximately 5-6% of the maximum average concentration measured for parent (approximately 100 ppb with wide variation). There was no analysis for other byproducts to possibly help explain the disappearance of parent. Other possible routes of dissipation such as plant interception or uptake (by algae, for example, for which a copper-based algicide was applied during the study to control algae in at least one pond); or horizontal or vertical flow or overflow of pond water from the ponds (pond hydrology) were not reported and apparently not considered. Therefore, from this study, the major routes of environmental dissipation of imazapyr are unknown. Since dissipation pathways were not determined by a self-consistent approach, no generalizations about dissipation can be made, and the apparent rapid disappearance of imazapyr could even have been an artifact of experimental procedures or of unknown, special conditions at the pond test sites. Any apparent dissipation "half-lives" for imazapyr are, therefore, essentially disappearance half-lives, serving only as a lower measure of potential longevity. Although the study author and reviewer sometimes went through the exercise of calculating and reporting apparent "half-lives" or DT50s, these are of uncertain/dubious value without an accounting for the loss and routing of imazapyr.

There were additional problems with the Florida pond results. In Florida, initially measured pond concentrations of imazapyr were only approximately 1/3 of the amount applied. In Missouri, the full application was recovered. For the Florida pond sediments, the reviewer also noted an apparent mix-up in sample numbering and analysis, apparently unnoticed by the study author and company technical staff. As given in greater detail below in the Comments section, it appears that the 0-3 inch depth sediment samples were not analyzed, and that the sediment results are probably those for the 3-6 inch depth. A different sediment sampling scheme was followed in Missouri (0-2 inch samples with no sub-sampling), and there was no such apparent mix-up in sample identification and analysis.

Overall this study did provide two reasonably clear results:

1) Parent imazapyr did not bioconcentrate appreciably in the fish and crayfish species tested (three fish and one crayfish species at each site, total of seven different species); however, there were no tests for degradates or their concentration in any of the test species. It should be noted that the reported limit of quantitation for parent in tissue was a relatively high 50 ppb. (In several instances, for unknown or unverified reasons, there was some limited mortality of some test species and/or their partial disappearance, such that for some sampling intervals there were insufficient amounts of tissue for analysis. However, this does not significantly alter the general conclusion of no appreciable bioconcentration of parent above a concentration of 50 ppb.)

2) Sediment concentrations of imazapyr in Missouri were effectively persistent for the entire study period of 180 days. During this time, the Missouri pond whose banks and entire water surface were treated (Missouri pond 21) maintained a sediment concentration of parent in the narrow range of approximately 10 to 18 ppb (see plot on page 376 of submission).

The following section of this DER briefly describes the study at each site, and summarizes their results. Subsequent sections provide increasing detail with much repetition from previous sections. Any use of this information is subject to the major limitations cited above and elsewhere in this report.

STUDY DESCRIPTION AND DATA SUMMARY

Field Dissipation - Aquatic

The aquatic field dissipation of imazapyr (CL 243997) was examined following application to two small, freshwater ponds in Florida (Seminole County) and two small, freshwater ponds in Missouri (Miller County). In no case was the geological or ecological nature of the ponds or whether the ponds were natural or manmade/constructed clearly stated; however, from various pieces of the descriptions and pond dimensions, the reviewer deduces that the ponds were probably constructed or significantly modified from a natural state (perhaps for the purposes of this or similar studies).

One test pond at each site received one application of imazapyr to the banks and outer edge (4-6 feet) of the test pond. Ponds treated in this manner in each state were designated as "**pond 11**." The other test pond at each site received one application to the banks and entire water surface of the test pond; these ponds were designated as "**pond 21**." In all cases, application rates were approximately 1.6 lb imazapyr acid equivalents (a.e.)/acre.

Pond waters were analyzed for parent and for two photodegradates of imazapyr. Pond sediments were analyzed for parent, but not for transformation products. As given below, three caged fish species and one caged crustacean species (Florida and Missouri species were different) were analyzed at each site for the presence of parent only (and at the relatively high limit of quantitation of 50 ppb).

The presence and nature of any plant life (non-target plants or target weeds) in any pond or pond bank and the effects of imazapyr on vegetation were not reported. There was no analysis for imazapyr or transformation products in plant material.

In Florida, prior to treatment, "previously established fish populations" (unspecified origin or former status) were removed from the two small ponds (pond dimensions of 54 x 199 feet or 54 x 190 feet, both with a depth of 25-27 inches). In place of the removed organisms, the following four non-target organisms, obtained from various extraneous sources, were added to the ponds: tilapia (*Tilapia aurea*; 2-8 inches in length), catfish (*Ictaburus nebulosus*; 6-8 inches in length), bluegill (*Lepomis spp.*; two years old), and crayfish (*Procambarus alleni*; 60-110 days old). These non-target organisms were placed in separate cages for each test species and held within each test pond. Imazapyr (Arsenal 2AS), mixed with Foam Buster® and diamond r surfactant (different mixture of adjuvants used at Missouri site), was broadcast applied once (August 13, 1996) at a nominal application rate of 1.6 lb acid equivalent (a.e.)/acre onto the two ponds.

In Missouri, unlike for Florida, there was no mention of removal of any resident fish populations prior to treatment, and the presence and status of any preexisting resident populations were not mentioned. Bass (*Micropterus salmoides*; one year old), catfish (*Italurus punctatus*; one year old), bluegill (*Lepomis macrochirus.*; two years old), and crayfish (*Cambarus diogenus*; 6 months old) from various extraneous sources were added to the two small test ponds (pond dimensions of 135 x 220 feet or 143 x 203 feet, both with a depth of 31-35 inches). The non-target organisms were placed in separate cages for each test species and held within each test pond. Imazapyr (Arsenal 2AS), mixed with Activator® (different mixture of adjuvants used at Florida site), was broadcast applied once (September 25, 1996) at a nominal application rate of 1.6 lb a.e./acre onto the two ponds.

Results from Florida Field Sites (FFS)

FFSPond 11. The imazapyr mixture (see above), broadcast applied once at a nominal application rate of 1.6 lb a.e./acre to the banks and outer edge (4-6 feet) of a small test pond (pond 11) of sand soil, dissipated with a DT50 of less than one day. However, because of cited study deficiencies, the apparent DT50 is of dubious value. Imazapyr was detected in the pond 11 **pond water** at a maximum concentration of 27.7 ppb at 0.2 days, ranged from 8.1 to 15.7 ppb from 0.3 to 5 days, decreased to 3.5 to 3.6 ppb by 7 to 14 days, and was <1.00 ppb by 42 days posttreatment. The degradates 2,3-pyridinecarboxylic acid (CL 9140) and 7-hydroxyfuro[3,4-b]pyridin-5(7H)-one (CL 119060) were not detected in the pond water above the limit of quantitation (2.00 ppb).

As noted above, for the Florida pond sediments, there was an apparent mix-up in sample numbering and analysis. As given in greater detail in the Comments section of this report, it appears that sub-samples from the 0-3 inch sediment depth were not analyzed, and that the results given by the study author for sediment are for the 3-6 inch sediment depth. Concentration of imazapyr in the pond 11 **sediment** (presumably in the 3-6 inch depth) was 2.6-2.9 ppb at 0.3 and 0.5 days, was a maximum of 4.3 ppb at 1 day, and was last detected at 1.0 ppb at 3 days posttreatment. *Pond sediment was not analyzed for degradates of imazapyr.* Imazapyr was not detected in the **fish or crayfish** above the relatively high limit of quantitation (50.0 ppb) at any sampling interval. There was no mention of plant life, and there was no analysis for residues of imazapyr or transformation products in plant material.

FFSPond 21. The imazapyr mixture, broadcast applied once at a nominal application rate of 1.6 lb a.e./acre to the banks and entire water surface of a small test pond (pond 21) of sand soil, dissipated with a reviewer-calculated half-life of 4.1 days ($r^2 = 0.93$) in the pond water. However, because of study deficiencies cited above, this "half-life" is of dubious value. Imazapyr was detected in the pond 21 **pond water** at a maximum concentration of 163.9 ppb at 0.5 days, ranged from 58.6 to 69.1 ppb from 1 to 3 days, decreased to 2.5 to 4.7 ppb by 14 to 22 days, and was <1.00 ppb by 29 days posttreatment. The degradate

2,3-pyridinecarboxylic acid (CL 9140)

was detected in the pond water at a maximum and final concentration of 5.3 ppb at 3 days posttreatment, and the degradate

7-hydroxyfuro[3,4-b]pyridin-5(7H)-one (CL 119060)

was detected in the pond water at a maximum concentration of 6.3 ppb at 5 days and a final concentration of 2.8 ppb at 7 days posttreatment. Imazapyr was detected in the pond 21 **sediment** at a maximum of 11.3 ppb at 0.3 days, decreased to 6.3 ppb by 3 days and 2.1 ppb by 14 days, and was last detected at 1.4 ppb at 29 days posttreatment (as previously noted, these results are presumably for the 3-6 inch sediment depth; by mistake, the 0-3 inch depth samples were apparently not analyzed). *Pond sediment was not analyzed for degradates of imazapyr.* Imazapyr was detected at an average of 636 ppb in bluegills, 233 ppb in tilapia, 68 ppb in catfish, and 59 ppb in crayfish at 0.2 days posttreatment, and was not detected above the limit of quantitation (50.0 ppb) at any other sampling interval. Plants or residues in plants were never mentioned.

Missouri Field Site (MFS)

MFSPond 11. The imazapyr mixture (see above), broadcast applied once at a nominal application rate of 1.6 lb a.e./acre to the banks and outer edge (4-6 feet) of a small test pond (pond 11) of silt loam soil, dissipated with an observed half-life of less than one day in the pond water; however, results were variable over time. Again, because of study deficiencies cited above, this "half-life" is of dubious value. Imazapyr was detected in the pond 11 **pond water** at a maximum concentration of 29.0 ppb at 0.1 days, was 8.3 ppb at 0.2 days, increased to 19.5 ppb by 2 days, decreased to 9.7 to 9.8 ppb by 5 to 7 days, was 2.9-4.1 ppb from 21 to 28 days, and was 1.5 ppb by 42 days posttreatment (the last sampling interval). The degradates 2,3-pyridinecarboxylic acid (CL 9140) and 7-hydroxyfuro[3,4-b]pyridin-5(7H)-one (CL 119060) were not detected in the pond water above the limit of quantitation (2.00 ppb). Imazapyr was detected in the pond 11 **sediment** at 33.7 ppb at 0.3 days, ranged from 1.4 to 3.2 ppb from 1 to 100 days, and was 4.5 ppb at 180 days posttreatment (the last sampling interval). *Pond sediment was not analyzed for degradates of imazapyr.* Imazapyr was not detected in the **fish or crayfish** above the limit of quantitation (50.0 ppb) at any sampling interval following the test application. There was no mention of plant life, and there was no analysis for residues of imazapyr or transformation products in plant material.

MFSPond 21. The imazapyr mixture (see above), broadcast applied once at a nominal application rate of 1.6 lb a.e./acre to the banks and entire water surface of a small test pond (pond 21) of silt loam soil, dissipated with a reviewer-calculated half-life of 15 days ($r^2 = 0.82$) in the pond water. Because of previously cited study limitations, this "half-life" is of dubious value. Within data variability, imazapyr was effectively persistent in the sediment; concentrations varied from approximately 10 to 18 ppb over the 180 day sediment test period. Imazapyr was detected in the pond 21 **pond water** at a maximum concentration of 196.1 ppb at 0.1 days, ranged from 140.5 to 164.4 ppb from 0.2 to 2 days, decreased to 103.1 to 117.2 ppb by 5 to 7 days and 69.0 ppb by 14 days, and was 25.2 ppb at 42 days posttreatment (the last sampling interval). The degradates 2,3-pyridinecarboxylic acid (CL 9140) and 7-hydroxyfuro[3,4-b]pyridin-5(7H)-one (CL 119060) were not detected in the pond water above the limit of quantitation (2.00 ppb).

Imazapyr was initially detected in the pond 21 **sediment** at 10.7 ppb, increased to a maximum of 17.7 ppb by 28 days, was 9.5-9.8 ppb from 42 to 100 days, and was 14.6 ppb at 180 days posttreatment (the last sampling interval). *Pond sediment was not analyzed for degradates of imazapyr*. Imazapyr was not detected in the **fish or crayfish** above the limit of quantitation (50.0 ppb) at any sampling interval following the test application. Plants or residues in plants were never mentioned.

MATERIALS AND METHODS

The aquatic field dissipation of imazapyr (CL 243997; 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)nicotinic acid), formulated as Arsenal 2AS (22.6% a.e.; Lot AC 8187-112A; Exhibit 1, p. 17; Exhibit 2, p. 338), was examined following application to two small ponds in Florida (Seminole County) and Missouri (Miller County). One test pond at each site received one application of imazapyr to the banks and outer edge (4-6 feet) of the test pond and the other test pond at each site received one application to the banks and entire water surface of the test pond.

Florida Field Site

Imazapyr (Arsenal 2AS), mixed with Foam Buster® and diamond r surfactant, was broadcast applied once (August 13, 1996) at a nominal application rate of 1.6 lb a.e./acre onto two small ponds (54 x 199 feet or 54 x 190 feet, both with a depth of 25-27 inches) of sand soil (0- to 6-inch depth: 97% sand, 1% silt, 2% clay, 2.0-3.3% o.m., pH 6.9-7.6; Leon, Debray, St. Johns Association; Exhibit 1, pp. 17-21). The application was made using a CO_2 backpack hand-held sprayer at a boom height of 18-32 inches over the soil or water. The test applications were made to the perimeter and pond surface edge (FFSpond 11) or to the perimeter and pond surface (FFSpond 21). Characteristics of the water were as follows for the two test ponds: pH 7.6-7.7, turbidity 0.52-2.52 NTU, and dissolved oxygen 10 ppm. An untreated control pond (pond 01) measured 54 x 199 feet with a depth of 25 inches, and was located 176 feet from the treated plots. A three-year site history indicated that the ponds were treated with Rodeo and copper algicide. Pond 11 was treated with copper (1 lb a.i./A) on August 27 and September 6, 13, and 24, 1996 for control of algae. Prior to treatment, previously established fish populations were removed from the ponds and tilapia (*Tilapia aurea*; 2-8 inches in length), catfish (*Ictaburus nebulosus*; 6-8 inches in length), bluegill (*Lepomis spp.*; two years old), and crayfish (*Procambarus alleni*; 60-110 days old) were added. The non-target organisms were placed in separate cages for each test species and held within each test pond (Exhibit 1, Appendix A, pp. 85-86). Cages were required to be a minimum of 4 x 4 x 4 ft in size for the fish and 1 x 4 x 4 for the crayfish. Historical mean annual precipitation and total water input during the study period were not reported.

Water samples were collected from the Florida treated ponds at 0.1, 0.2, 0.3, 0.5, 1, 2, 3, 5, 7, 14, 22, 29, and 42 days posttreatment and following rainfall events on 3, 27, 30, and 36 days posttreatment (Exhibit 1, Table II, pp. 51 and 53). Sediment (0- to 6-inch depth) samples were collected from the treated ponds at 0.3, 0.5, 1, 3, 7, 14, 22, 29, 42, 91, and 178 days posttreatment (Exhibit 1, Table III, p. 55). Non-target organisms were collected from the treated ponds at 0.2, 1, 3, 7, 14, 22, 29, and 42 days posttreatment (Exhibit 1, Table IV, p. 57).

Sediment and water samples were collected from five sampling stations established in each of the treated test ponds at the Florida test site (Exhibit 1, pp. 21-22, Appendix A, pp. 86-97 and 89-91). Three stations were located to best divide the pond into thirds for sampling and two stations were located between 1-3 feet from the water edge. At the designated sampling intervals, three aquatic sediment cores were randomly collected from each of the five sampling stations in each test pond to a depth of 6 inches. Sediment samples were collected using a zero contamination handheld probe or a bucket auger sediment sampler. Each sediment core was sub-sampled into 0- to 3-inch and 3- to 6-inch sections; cores were composited by sampling station and depth. Water samples were collected at the designated sampling intervals and following a rainfall event, defined as 0.25 inches of rain occurring in less than four hours. At designated sampling events, four 1-liter water samples were collected from each of the five sampling stations from mid-depth of the water column using a spring loaded sampler. Following a rainfall event, four 1-liter water samples were collected from the two sampling stations closest to the waters edge. Sediment and water samples were collected from the control pond from a single sampling station located at the center of the pond. Approximately 1 lb of each fish and crayfish species was collected from each treated pond at the designated sampling intervals and frozen. Fish and crayfish were sampled by hand using a net to remove them from their cages.

<u>Missouri Field Site</u>

Imazapyr (Arsenal 2AS), mixed with Activator®, was broadcast applied once (September 25, 1996) at a nominal application rate of 1.6 lb a.e./acre onto two small ponds (135 x 220 feet or 143 x 203 feet, both with a depth of 31-35 inches) of silt loam soil (0- to 2-inch depth: 30-32% sand, 51-53% silt, 17% clay, 0.9% o.m., pH 6.5-6.8; Exhibit 2, pp. 338-341). The application was made using a CO_2 backpack hand-held sprayer at a boom height of 27-29 inches over the soil or water. The test applications were made to the perimeter and pond surface edge (pond 11) or to the perimeter and pond surface (pond 21). Characteristics of the water were as follows for the two test ponds: pH 7.1-7.4, turbidity 0.62-1.9 NTU, and dissolved oxygen 4.7-7.4 ppm. An untreated control pond (pond 01) measured 144 x 197 feet with a depth of 33 inches, and was located 327 feet from the treated plots. A three-year site history indicated that the ponds were not treated with any pesticides. No maintenance pesticides were used during the study period. Prior to treatment, bass (*Micropterus salmoides*; one year old), catfish (*Italurus punctatus*; one year old), bluegill (*Lepomis macrochirus*.; two years old), and crayfish (*Cambarus diogenus*; 6 months old) were added to the test ponds. The non-target organisms were placed in separate cages for each test species and held within each test pond (Exhibit 2, Appendix A, pp. 401-402). Cage dimensions were not specified. Historical mean annual precipitation and total water input during the study period were not reported.

Water samples were collected from the Missouri treated ponds at 0.1, 0.2, 0.3, 1, 2, 3, 5, 7, 14, 21, 28, and 42 days posttreatment and following rainfall events on 26, 27, and 41 days posttreatment (Exhibit 2, Table II, pp. 370 and 372). Sediment (0- to 2-inch depth) samples were collected from the treated ponds at 0.3, 1, 3, 7, 14, 21, 28, 42, 100, and 180 days posttreatment (Exhibit 2, Table III, p. 374). Non-target organisms were collected from the treated ponds at 0.2, 1, 3, 7, 14, 21, 28, and 42 days posttreatment (Exhibit 2, Table I, pp. 365-369).

Sediment and water samples were collected from ten sampling stations established in each of the treated test ponds at the Missouri test site (Exhibit 1, p. 342, Appendix A, pp. 402-403 and 405-407). Six stations were located to best divide the pond into sixths for sampling and four stations were located between 1-3 feet from the water edge; the ten stations were paired into sets for compositing purposes. At the designated sampling intervals, two aquatic sediment cores were collected from two randomly selected points near each sampling station in each test pond to a depth of 2 inches; cores were composited by each sampling station pair. Sediment samples were collected using a zero contamination handheld probe. Water samples were collected at the designated sampling intervals and following a rainfall event, defined as 0.25 inches of rain occurring in less than four hours. At designated sampling events, two 1-liter water samples were collected from each of the ten sampling stations from mid-depth of the water column using a spring loaded sampler; water samples were composited by each station pair. Following a rainfall event, four 1-liter water samples were collected from two of the sampling stations closest to the waters edge. Sediment and water samples were collected from the control pond from a single sampling station located at the center of the pond. Approximately 1 lb of each fish and crayfish species was collected from each treated pond at the designated sampling intervals and frozen. Fish and crayfish were sampled by hand using a net to remove them from their cages.

To assess the homogeneity and stability of the test substance during application, a sample of the tank mix was collected before and after the test application at each test site (Exhibit 1, p. 21; Exhibit 2, p. 341). Spray mixture samples were placed into frozen storage within 2 hours (Florida test site) or 13 hours (Missouri test site) of sampling, and shipped frozen to the analytical laboratory. The mean concentration of the parent in the tank mix was 87-88% of the expected at the Florida site and 98.2-102.0% of the expected at the Missouri site (Exhibit 1, Table V, p. 58; Exhibit 2, Table IV, p. 377).

Sediment samples from both test sites were shipped to Cyanamid Agricultural Research Center to be sieved and homogenized and then shipped to Centre Analytical Labs for analysis (Exhibit 1, pp. 22-25; Exhibit 2, pp. 343-345). Sediment samples were analyzed for imazapyr according to American Cyanamid Method M 3014 (Exhibit 1, pp. 169-203; Exhibit 2, pp. 611-646). Sediment samples were extracted with sodium hydroxide followed by solvent partitioning and solid phase extraction cleanup. Extracts were analyzed by Capillary Electrophoresis, which consisted of an Applied Biosystems Model 270A-HT Capillary Electrophoresis System with a Hewlett Packard Chemstation data acquisition system. The limit of quantitation for imazapyr in sediment was 1.0 ppb. Mean concurrent recoveries from sediment samples fortified with imazapyr at 1-500 ppb were $84 \pm 11.3\%$ and $86 \pm 16.7\%$ for the Florida and Missouri test samples, respectively.

Pond water samples were shipped directly to Centre Analytical Labs and analyzed for imazapyr, 7-hydroxyfuro[3,4-b]pyridin-5(7H)-one (CL 119060), and 2,3-pyridinecarboxylic acid (CL 9140; Exhibit 1, pp. 22-25; Exhibit 2, pp. 343-345). Pond water samples were analyzed for imazapyr according to American Cyanamid Method M 3001 (Exhibit 1, pp. 204-259; Exhibit 2, pp. 564-610) and analyzed for CL 119060 and CL 9140 according to American Cyanamid Methods M 2672 and 3097, respectively (Exhibit 1, pp. 260-286; Exhibit 2, pp. 506-563). Imazapyr was extracted from the pond water samples by acidifying, passing through a quaternary amine strong anion exchange solid phase extraction cartridge, and trapping onto a C18-OH solid phase extraction cartridge. Imazapyr was then eluted using methanol onto a benzenesulfonic acid strong cation exchange cartridge and then eluted from that cartridge using potassium phosphate. The analyte was then acidified, partitioned into methylene chloride, and the solvent evaporated. After redissolving in water, the analyte was loaded onto a Bond Elut LMS column and eluted with methanol. Following the evaporation of the solvent, the residue was dissolved in water and analyzed by Capillary Electrophoresis as previously described for the sediment samples. The limit of quantitation for imazapyr in pond water was 1.0 ppb. Mean concurrent recoveries from pond water samples fortified with imazapyr at 1-450 ppb were 87 ± 12% and 88 ± 8.2% for the Florida and Missouri test samples, respectively. CL 119060 and CL 9140 were extracted from the pond water samples by acidifying, passing through a MF-C18 solid phase extraction cartridge, and trapping onto a ENV+ solid phase extraction cartridge. The analytes were then eluted using methanol and passed through a CBA cartridge. CL 119060 was analyzed by HPLC with positive ion electrospray ionization using Mass Spectroscopy Detection and CL 9140 was analyzed by Capillary Electrophoresis as previously described. The limit of quantitation for CL 119060 and CL 9140 in pond water was 2.0 ppb. Mean concurrent recoveries from pond water samples fortified with CL 119060 and CL 9140 at 2-20 ppb were 76.2 ± 7.7% and 84.6 ± 18.4%, respectively, for the Florida test samples, and 78 ± 9.4% and 95 ± 11.1%, respectively, for the Missouri test samples.

Fish and crayfish from both test sites were shipped to Cyanamid Agricultural Research Center for homogenization of the fish fillets and crayfish tails with dry ice and then shipped to Maxim Technologies Incorporated for analysis (Exhibit 1, pp. 22-23; Exhibit 2, p. 343). Homogenized samples were analyzed for imazapyr according to American Cyanamid Draft Method M 3066 (Exhibit 1, p. 24, Appendix B, pp. 155-168; Exhibit 2, p. 344, Appendix B, pp. 492-505). The samples were analyzed by Capillary Electrophoresis, which consisted of a Hewlett Packard HP ^{3D}CE Capillary Electrophoresis System, Model G 1600AX and a Hewlett Packard Chemstation Integrator. The limit of quantitation was 50 ppb. Mean concurrent recoveries from samples fortified with imazapyr at 50-1000 ppb (Florida test site) or 50-500 ppb (Missouri test site) were 81.1 ± 5.7% and 82.6 ± 6.4%, respectively.

RESULTS/DISCUSSION

Florida Field Site

Imazapyr (Arsenal 2AS), broadcast applied once at a nominal application rate of 1.6 lb a.e./acre to the banks and outer edge (4-6 feet) of a small test pond (pond 11) of sand soil, dissipated with a DT50 of less than one day. However, because of cited study deficiencies, the apparent DT50 is of dubious value. Imazapyr was detected in the pond 11 **pond water** at a maximum concentration of 27.7 ppb at 0.2 days, ranged from 8.1 to 15.7 ppb from 0.3 to 5 days, decreased to 3.5 to 3.6 ppb by 7 to 14 days, and was <1.00 ppb by 42 days posttreatment (Exhibit 1, Table II, p. 51). The degradates 2,3-pyridinecarboxylic acid (CL 9140) and 7-hydroxyfuro[3,4-b]pyridin-5(7H)-one (CL 119060) were not detected in the pond water above the limit of quantitation (2.00 ppb). Imazapyr was detected in the pond 11 **sediment** at 2.6-2.9 ppb at 0.3 and 0.5 days, was a maximum of 4.3 ppb at 1 day, and was last detected at 1.0 ppb at 3 days posttreatment (Exhibit 1, Table III, p. 55). Pond sediment was not analyzed for degradates of imazapyr. Imazapyr was not detected in the **fish or crayfish** above the limit of quantitation (50.0 ppb) at any sampling interval (Exhibit 1, Table IV, p. 57).

Imazapyr (Arsenal 2AS), broadcast applied once at a nominal application rate of 1.6 lb a.e./acre to the banks and entire water surface of a small test pond (pond 21) of sand soil, dissipated with a reviewer-calculated half-life of 4.1 days ($r^2 = 0.93$) in the pond water. However, because of cited study deficiencies, this "half-life" is of dubious value. Imazapyr was detected in the pond 21 **pond water** at a maximum concentration of 163.9 ppb at 0.5 days, ranged from 58.6 to 69.1 ppb from 1 to 3 days, decreased to 2.5 to 4.7 ppb by 14 to 22 days, and was <1.00 ppb by 29 days posttreatment (Exhibit 1, Table II, p. 53). The degradate

2,3-pyridinecarboxylic acid (CL 9140)

was detected in the pond water at a maximum and final concentration of 5.3 ppb at 3 days posttreatment, and the degradate

7-hydroxyfuro[3,4-b]pyridin-5(7H)-one (CL 119060)

was detected in the pond water at a maximum concentration of 6.3 ppb at 5 days and a final concentration of 2.8 ppb at 7 days posttreatment. Imazapyr was detected in the pond 21 **sediment** at a maximum of 11.3 ppb at 0.3 days, decreased to 6.3 ppb by 3 days and 2.1 ppb by 14 days, and was last detected at 1.4 ppb at 29 days posttreatment (Exhibit 1, Table III, p. 55). Pond sediment was not analyzed for degradates of imazapyr. Imazapyr was detected at an average of 248.8 ppb in the **fish and crayfish** samples at 0.2 days posttreatment, and was not detected above the limit of quantitation (50.0 ppb) at any other sampling interval (Exhibit 1, Table IV, p. 57).

Missouri Field Site

Imazapyr (Arsenal 2AS), broadcast applied once at a nominal application rate of 1.6 lb a.e./acre to the banks and outer edge (4-6 feet) of a small test pond (pond 11) of silt loam soil, dissipated with an observed DT50 of less than one day in the pond water; however, results were variable over time and the DT50 is of dubious value. Imazapyr was detected in the pond 11 **pond water** at a maximum concentration of 29.0 ppb at 0.1 days, was 8.3 ppb at 0.2 days, increased to 19.5 ppb by 2 days, decreased to 9.7 to 9.8 ppb by 5 to 7 days, was 2.9-4.1 ppb from 21 to 28 days, and was 1.5 ppb by 42 days posttreatment (the last sampling interval; Exhibit 2, Table II, p. 370). The degradates 2,3-pyridinecarboxylic acid (CL 9140) and 7-hydroxyfuro[3,4-b]pyridin-5(7H)-one (CL 119060) were not detected in the pond water above the limit of quantitation (2.00 ppb). Imazapyr was detected in the pond 11 **sediment** at 33.7 ppb at 0.3 days, ranged from 1.4 to 3.2 ppb from 1 to 100 days, and was 4.5 ppb at 180 days posttreatment (the last sampling interval; Exhibit 2, Table III, p. 374). Pond sediment was not analyzed for degradates of imazapyr. Imazapyr was not detected in the **fish or crayfish** above the limit of quantitation (50.0 ppb) at any sampling interval following the test application (Exhibit 2, p. 345).

Imazapyr (Arsenal 2AS), broadcast applied once at a nominal application rate of 1.6 lb a.e./acre to the banks and entire water surface of a small test pond (pond 21) of silt loam soil, dissipated with a reviewer-calculated half-life of 15 days ($r^2 = 0.82$) in the pond water. Because of previously cited study limitations, this "half-life" is of dubious value. Within data variability, imazapyr was effectively persistent in the sediment; concentrations varied from approximately 10 to 18 ppb over the 180 day sediment test period. Imazapyr was detected in the pond 21 **pond water** at a maximum concentration of 196.1 ppb at 0.1 days, ranged from 140.5 to 164.4 ppb from 0.2 to 2 days, decreased to 103.1 to 117.2 ppb by 5 to 7 days and 69.0 ppb by 14 days, and was 25.2 ppb at 42 days posttreatment (the last sampling interval; Exhibit 2, Table II, p. 372). The degradates 2,3-pyridinecarboxylic acid (CL 9140) and 7-hydroxyfuro[3,4-b]pyridin-5(7H)-one (CL 119060) were not detected in the pond water above the limit of quantitation (2.00 ppb). Imazapyr was initially detected in the pond 21 **sediment** at 10.7 ppb, increased to a maximum of 17.7 ppb by 28 days, was 9.5-9.8 ppb from 42 to 100 days, and was 14.6 ppb at 180 days posttreatment (the last sampling interval; Exhibit 2, Table III, p. 374). Pond sediment was not analyzed for degradates of imazapyr. Imazapyr was not detected in the **fish or crayfish** above the limit of quantitation (50.0 ppb) at any sampling interval following the test application (Exhibit 2, p. 345).

DEFICIENCIES/DEVIATIONS

1. For the Florida ponds, initially measured concentrations of imazapyr were only approximately 1/3 of the expected (approximate values for pond 11: measured 93 ppb versus expected 262 ppb; for pond 21: measured 25 ppb versus expected 75 ppb). The full application was recovered in Missouri.

2. For the Florida field sites, the reviewer noticed an apparent mix-up in identification and subsequent laboratory analysis of sediment samples. As described in the Materials and Methods section above, at designated sampling intervals, three aquatic sediment cores were randomly collected from each of five sampling stations in each test pond to a depth of 6 inches. Each sediment core was sub-sampled into 0- to 3-inch and 3- to 6-inch sections; cores were composited by sampling station and depth (5 sampling stations x 2 depths for each = total of 10 samples for each sampling interval). According to study Appendix A (study protocol, amendments, and deviations), the protocol amendment on page 111 (renumbered from 107) corrects previous sample numbers to reflect the two sub-samples by adding the suffix "A" to the 0-3 inch sections, while retaining the original sample number for the 3-6 inch sections. However, in all tables for sediment analysis results there are only 5 values listed for each interval, rather than 10, and the 5 listed samples do not have the "A" suffix. Although it remains ambiguous, it is reasonable to infer that the sediment results discussed in the submission and in this report are those for the 3-6 inch sections (those without the "A" suffix); apparently, the 0-3 inch sections, which presumably would have higher concentrations than the 3-6 inch sections, were overlooked.

   Numerous, compound protocol amendments (30) and deviations (8), given in study Exhibit 1, Appendix A, may have been responsible for the apparent sample confusion. Although there were also numerous, compound protocol amendments (29) and deviations (16) for the Missouri sites (study Exhibit 2, Appendix A), there was no comparable confusion for sediment samples because only 0-2 inch sediment samples were collected and analyzed, and these were not sub-sampled. The many irregularities, exceptions, and alterations to planned study procedures made review tedious and detracted from study integrity.

3. The registrant calculated half-lives of 3.9 days in the Florida Pond 21 pond water and 15 days in the Missouri Pond 21 pond water (Exhibit 1, p. 25; Exhibit 2, pp. 345-346). No other half-lives were reported by the registrant. As the reviewer stated prominently in the Scientific Conclusions section of this report, any such "half-lives" are essentially without meaning in the context of the study.

4. The study author stated that a frozen storage stability study investigating the stability of imazapyr (CL 243997) in pond water, sediment, and non-target organisms and the stability of CL 9140 and CL 119060 in pond water was ongoing (Exhibit 1, p. 23; Exhibit 2, p. 344). Interim stability data were not provided in this report. Test samples were stored for a maximum of 27 months for pond water and 21 months for pond sediment and non-target organisms.

5. The study author stated that an inversion of the Missouri test ponds was noted approximately two weeks prior to application of the test substance, and caused a fish kill and an increase in the amount of sediment suspended in the ponds (Exhibit 2, pp. 345-

346). The author also noted that light penetration was limited to the upper few inches of the ponds and resulted in a potential decrease in photolytic degradation and increase in the half-life of imazapyr.

6. It was reported that supplemental irrigation was supplied to the ponds at the Florida test site on an as needed basis in order to maintain healthy fish and crayfish (Exhibit 1, p. 21), and that the Missouri ponds were not irrigated during the study period (Exhibit 2, p. 341).

7. The two test sites were chosen because they represent an area of the country where Arsenal 2AS herbicide is intended for use in a major use area of the United States (Exhibit 1, p. 17; Exhibit 2, p. 338).