

108501 (Prowl)
SHAUGHNESSEY NO.

+ pend: methalin 108501

31
REVIEW NO.

in tank mix with 028201
Stam M-4

EEB BRANCH REVIEW

IN 2/4/81 OUT 4/21/81

FILE OR REG. NO. 241-243

PETITION OR EXP. PERMIT NO. 012401

DATE OF SUBMISSION 1/19/81

DATE RECEIVED BY HED 1/30/81

RD REQUESTED COMPLETION DATE 4/5/81

EEB ESTIMATED COMPLETION DATE

RD ACTION CODE/TYPE OF REVIEW 335/Amendments

TYPE PRODUCT(S): I, D, H, F, N, R, S Herbicide

DATA ACCESSION NO(S).

PRODUCT MGR. NO. R. Taylor (25)

PRODUCT NAME(S) Prowl Herbicide / Stam M-4

COMPANY NAME American Cyanamid Company

SUBMISSION PURPOSE Proposed conditional registration of rice use

for Prowl (pendimethalin) in tank mix with propanil

SHAUGHNESSEY NO.	CHEMICAL & FORMULATION	% A.I.
108501	(Prowl or pendimethalin)	42.3
	(N-(1-ethylpropyl)-3-4-	
	dimethyl-2,6-dinitro-	
	benzenamine)	

Pesticide Label Information (from Supplemental labeling for
Registration No. 241-243-AA)

To be used on dry seeded rice in all states except California. Not to be used in water-seeded rice*.

General Information

PROWL plus STAM M-4 is a postemergence treatment which combines the direct contact action of STAM M-4 and the residual activity of PROWL. Since the residual activity of PROWL provides preemergence control of certain annual grasses which can germinate after this tank-mix treatment is applied, flooding after application can be delayed.

For maximum weed control with this treatment, it is important to carefully follow the directions below for (1) adequate spray coverage of weeds and soil and (2) proper timing of application, when barnyardgrass (watergrass) is in the 1 to 3 leaf stage of growth with an occasional 4 leaf plant (make application when sprangletop is less than 1/2 inch in height).

Spraying Instructions

AERIAL APPLICATIONS

For aerial application, apply the recommended rate in 10 to 12 gallons of water per acre to insure adequate coverage. Refer to leaflet on top of PROWL container for mixing instructions. To minimize drift (see STAM M-4 label for sensitive crops), DO NOT apply during periods of gusty winds or winds in excess of 5 mph. Uniform spray distribution may not be achieved when wind velocity is greater than 5 mph. It is recommended that a flagman or an automatic mechanical flagging unit on the aircraft be used to avoid overlapping and possible crop injury.

GROUND APPLICATIONS

For ground equipment, apply the recommended rate in 15 to 20 gallons of water per acre to insure adequate coverage. Refer to leaflet on top of PROWL container for mixing instructions. Use a properly calibrated low-pressure (20 to 40 psi) sprayer equipped with 8002 or larger size Tee-Jet or comparable nozzles to achieve uniform spray distribution and minimize drift. Keep the by-pass line on or near

*Reviewer's Note: Wet-seeded rice is broadcast from airplanes when the fields are flooded. Dry seeded rice is planted when the fields are dry (personal communication with Charles Lewis of EEB).

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the bottom of the tank to minimize foaming. Nozzle screens must be no finer than 50 mesh. DO NOT apply PROWL during periods of gusty winds or when velocity is greater than 10 mph.

Early Postemergence Applications

The seedbed should be firm and free of clods and trash. The seedbed must be prepared to allow for good seed coverage. Previous crop residues should be thoroughly mixed into the soil to a depth of 4 to 6 inches by plowing or disking before planting rice.

Uniformly apply recommended PROWL + STAM M-4 treatment by aircraft or ground equipment after rice emergence, according to spraying instructions above, when barnyardgrass is in the 1 to 3 leaf growth stage with an occasional 4 leaf plant (make application when sprangletop is less than 1/2 inch). THE GROWER SHOULD INSPECT FIELDS FREQUENTLY TO CHECK GROWTH OF BARNYARDGRASS AND/OR SPRANGLETOP TO DETERMINE PROPER APPLICATION TIMING. Timing of applications should be based on the growth stage of barnyardgrass and/or sprangletop and not on the growth stage of rice. If rice is too small to maintain a flood on the field, the treatment can still be applied since flooding can be delayed because of the residual activity of PROWL.

While the residual activity of PROWL allows flooding to be delayed, proper water management practices must be followed for normal rice growth. Flooding should not be delayed if weeds begin to develop after application.

Since soil and weeds must be completely exposed to spray coverage, no flood water should be on field at time of application. If necessary, fields may be flushed prior to treatment to produce vigorous rice and weed growth.

* Since the residual activity of PROWL is activated by moisture, PROWL is most effective in controlling emerging weeds when adequate rainfall or irrigation (flush) is received within 7 days after application.

For maximum direct contact activity of STAM M-4, delay application if there is a chance of rain within 6 to 8 hours.

PROWL plus STAM M-4 tank mixture provides direct contact control of weeds listed on the STAM M-4 label. The following grass species are controlled by the residual activity of PROWL plus STAM M-4 tank mixture at the rates recommended for each soil texture listed below:

Barnyardgrass (watergrass) (Echinochloa crus-galli or Echinochloa colonum)

Crabgrass (Digitaria spp.)

Signalgrass (Brachiaria platyphylla)

Sprangletop (Leptochloa spp.)

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Broadcast Rate Per Acre of PROWL
Plus STAM M-4

Soil Texture	PROWL + STAM M-4**
COARSE	
sandy loams	1.5 pts + 6.0 to 8.0 pts
MEDIUM	
loams, silts, silt loams	1.5 to 2.0 pts + 6.0 to 8.0 pts
FINE	
silty clay loams*, sandy clay loams*, clay loams, silty clays, clays	1.5 to 2.0 pts + 6.0 to 8.0 pts

* Sometimes considered transitional soils and may be classified as either fine or medium textured soils.

**Reviewer's Notes: 1.5 to 2.0 pts PROWL = 0.75 - 1 lb. pendimethalin a.i. (PROWL is 44% a.i. or 4 lb. a.i./gal.). STAM M-4 is applied at 6.0 - 8.0 pts/acre or 3.0 - 4 lbs. a.i. propanil per acre.

④

The high rate of PROWL for medium and fine textured soils should be used if heavy weed populations are present. The high rate of STAM M-4 should be used in the following situations at the time of application: (1) in case of unseasonably cool weather, (2) if barnyardgrass has progressed to predominantly the 3 to 4 leaf stage, or (3) if emerged sprangletop (less than 1/2 inch) is present.

DO NOT apply this tank mixture within 14 days before or after insecticide applications because serious damage to rice may occur.

DO NOT apply this tank mixture in liquid fertilizer.

DO NOT make more than one application of PROWL per season.

DO NOT use rice straw from PROWL-treated fields to feed livestock.

PROWL-treated land can be planted to other crops the following year.

Observe all precautions and limitations on the STAM M-4 label.

Propanil is currently registered for use on rice at a maximum rate of 6.0 lb. a.i./acre (see 3 February 1981 Residue Chemistry review).

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Physical and Chemical Properties

Chemical Name

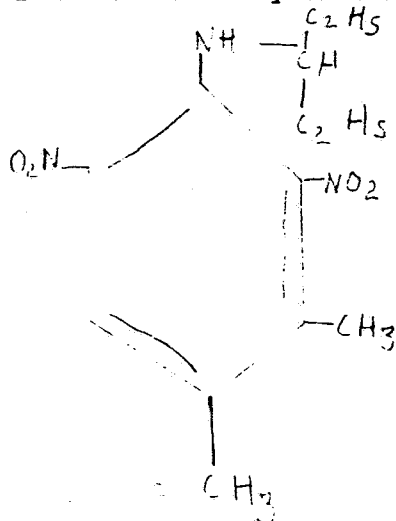
Prowl = Pendimethalin (N-(1-ethylpropyl)-3,4-dimethyl-2,6-dinitrobenzenamine)

Propanil = 3',4'-Dichloropropionanilide

101.2

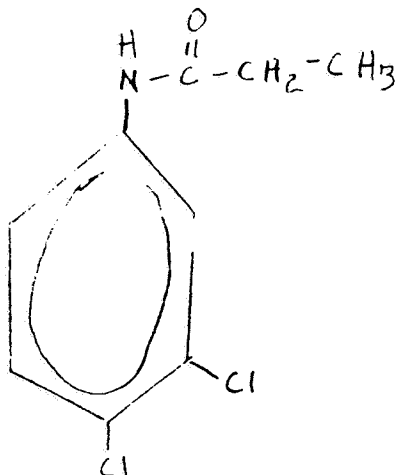
Structural Formula

Pendimethalin (from 1979 Weed Society Manual)



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Propanil (12/3/79 review by John Leitzke)



101.7 Solubility

Propanil - 500 ppm in 87°C water. Kearny, P. C. and D. P. Kaufman. 1976. Herbicides. Chemistry, Degradation and Mode of Action. Second addition. Marcel Dekker, Inc. New York and Basel. p. 613.

Acetone solubility is 699 ppm at 26°C (See B. Roberts' 10/23/79 review).

Pendimethalin (from L. Touart's 5/13/80 review)

<u>Solvent</u>	<u>Temperature °C</u>	<u>Solubility (g/l)</u>
Water	23	0.5
Acetone	26	699
Xylene	26	628
Isopropanol.	26	77
Corn Oil	26	148

102 Behavior in the Environment - Pendimethalin

General (from W. Roberts' 10/23/79 review):

Soil metabolism - anaerobic metabolism of parent is more rapid than aerobic metabolism but breakdown products are more rapidly metabolized aerobically than anaerobically.

Soil persistence - halflife of PROWL is 12-16 months.

Hydrolysis - PROWL is stable at pH 5, 7, and 9 at 25°C in dark.

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Photolysis - Soil TLC - 33 - 56% of applied activity lost in 8 weeks, while 87% of applied activity is lost from glass slides in 24 hours. No volatilization from water solution but all parent is degraded in 1 week.

Microbial - Microbes do not degrade parent nor does PROWL affect microbe activities.

102.1 Soil

The following is from a 18 June 1980 memo from David Severn to Clayton Bushong:

"... PROWL or its degradates are not expected to leach to any significant degree under environmental conditions."

Behavior in the Environment - Propanil

(See 12/3/79 wheat review by John S. Leitzke for details of information abstracted below.)

Soil - 1/2-life of 30 to 40 days. Soil metabolites TCAB 3,3',4,4'- tetrachloroazobenzene and 3,3',4'-trichloro-4-(3,4-dichloroanilino)- azobenzene are potential carcinogens.

Water - At pH 5.1 over 56% of propanil was hydrolyzed in buffered solutions to 3,4-dichloroaniline after 28 days at ca. 25°C. Under similar conditions, over 99% of propanil was still present at pH 7.2 and 8.9. No TCAB was detected.

Animal - In bioaccumulation studies during which the propanil concentrations were continually renewed, the highest biomagnification factors

$$\left(\frac{\text{concentration in body tissue}}{\text{concentration in water}} \right)$$

were as follows for crayfish and catfish:

Catfish Viscera - 170x
Crayfish Tails - 12x

Plants - Hydrolysis of propanil in plants is a key to the selectivity of the herbicide. A high percentage of [¹⁴C] propanil applied to peas and rice was converted to ¹⁴CO₂.

[from Nishimura and Takamiya (1966) cited in Ashton and Crafts (1973)]

Propanil is metabolized in rice to 3,4-dichloroaniline and propionic acid. In susceptible plants, it is metabolized into 3,4-dichlorolactanilide.

Propanil inhibits photosynthesis by reduction of cytochrome 553. Nishimura and Takamiya (1966) cited in Ashton and Crafts (1973), p. 140.

Ashton, F. M. and A. S. Crafts. 1973. Mode of action of herbicides. John Wiley and Sons. New York, NY

Nishimura, M. and A. Takamiya. 1966. Porphyrin. Biochem. Biophys. Acta. 120:45-56.

103 Toxicological Properties - Propanil

With this registration application, American Cyanamide submitted only a pendimethalin crayfish toxicology study in the way of fish and wildlife information. The toxicology data, other than those for crayfish, represent the values for each major taxonomic group (mammals, birds, fish, aquatic invertebrates, and terrestrial insects) which are valid and would most detract from favorable consideration of this registration.

103.1 References from Toxicology Branch

Chronic rat NOEL = 400 ppm STAM

103.2.2 Avian Toxicity - Stampede (Propanil)

Mallard LD₅₀ for birds receiving oral doses on 10 successive days was 375 mg/kg/day [Supplemental study reviewed by F. Betz (10/10/78)].

103.4 Aquatic Toxicity - Stampede (Propanil)

Aquatic acute toxicity values ranged from 4.8 to 22.4 ppm in F. Betz's (10/10/78) review.

Chronic Toxicity to Fish - Propanil

A fathead minnow embryo-larval study conducted by Dan Call at the University of Wisconsin - Superior supported a Maximum Acceptable Toxicant Concentration (MATC), or no effect level, of 0.4 - 0.6 ppb A.I. Dan Call's results were disputed by Rohm and Haas on the basis of the treatment chemical being contaminated with TCAB (3,3',4,4'-tetrachloroazobenzene) and TCAzoB (3,3',4'-trichloro-4-(3,4-dichloroaniline)-azobenzene. Dividing the application factor generated with the fathead minnow embryo-larval study into the theoretical 96-hr. LC₅₀ generates a potential coldwater species MATC of 0.083 ppb (see John S. Leitzke's 12/11/80 "Note to the Propanil file").

103 Toxicological Properties - Pendimethalin

The following toxicological values are representative and not comprehensive. The registrant submitted only a crayfish toxicity

study in regard to environmental safety information to support this amendment. See Bill Robert's 10/23/79 review for a more complete listing of toxicological values.

103.1 References from Toxicology Branch - Prowl (Pendimethalin)

Dermal LD₅₀ (Rabbits) - 5000 mg/kg - 93% tech.

Inhalation LC₅₀ Rats - 15% aqueous solution fog - 320 mg/l (nominal concentration).

Dermal Irritation - Rabbits - No irritation from 93% technical.

Rat - 90 day NEL - 500 ppm

103.2 Avian Acute Oral LD
50

(All avian data validations are by L. Windberg 9/22/77). Mallard duck acute oral 1421 mg/kg.

103.2.2 Avian Dietary LC 's
50

Mallard duck	10,388	Core
Bobwhite quail	4,187 ppm	Core

103.2.3 Aquatic Toxicity Studies - Pendimethalin

From W. Robert's 10/23/79 review.

The 96 hr. LC₅₀'s below are for the technical formulation (93.2%).

Rainbow trout	1.00 ppm
Channel catfish	0.42 ppm

103.2.4 Aquatic Invertebrate LC
50

Daphnia magna 0.28 ppm

Data Evaluation Record

Reviewer: Robert K. Hitch. Ecological Effects Branch, CM #4, (703) 557-5600.

Chemical: 108501 Pendimethalin
94.2%

Citation: ABC (Analytical BioChemistry Laboratories) Inc., 1980. Acute toxicity of AC 92,553 to the freshwater crayfish (Procambarus simulans). Static acute bioassay final report #25725.

EPA Accession #099889

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Type of Study: 96 hr. LC₅₀ with an aquatic invertebrate.

Reviewer's Abstract of Study:

<u>Test Organism</u> <u>Weight & Length</u>	The crayfish averaged in length (The length measurement was made from tip of rostrum to tip of tail) 43.3 (+ 3.2) mm and in weight 2.46 (+ 0.90) grams.
<u>Feeding Regime</u>	Feeding of the crayfish was terminated 48 hrs. before study commencement.
<u>Dilution</u> <u>Water</u>	The dilution water was soft reconstituted as described in Stephan (1975).
<u>Temperature</u> <u>Loading</u>	The test temperature was 22°C. The tests were conducted in 40 liter glass vessels containing 30 liters of soft reconstituted water.
<u>Treatment</u> <u>Levels</u>	Ten crayfish were tested in a preliminary 72 hr. test. Mortalities in this test were 10, 20, and 10% after exposure at 1,000, 10,000 and 100,000 ppb, respectively. In the definitive 96 hr. study, 20% mortality occurred at 56,000 ppb and among the triplicate 300,000 ppb test vessels, percentage mortalities were recorded as 10, 0, and 20.

Reviewer's Conclusions:

If the registrant is willing to accept the LC₅₀ as being greater than 1,000 ppb (1.0 ppm), then the study will be judged "supplemental" and capable of supporting the current registration. It was not judged "core" and capable of meeting general requirements for a freshwater invertebrate LC₅₀ in regard to basic study requirements because of deviations from standard test methods noted below. The reasons for still considering the study capable of supporting this rice registration in spite of the deviations are also noted below.

1. The dissolved oxygen level was less than 40% of saturation in some of the high concentrations (300,000 ppb). The study was still judged to be of value as these concentrations are orders of magnitude above the EEC and because, generally, a lower D.O. would tend to stress a test organism and make it succumb to a toxicant more readily.
2. DMSO was used as a solvent. This was acceptable to this reviewer, although not recommended by Stephan (1975) because this solvent would also tend to increase mortalities rather than decrease them.
3. The compound was noted to form a yellow precipitate at test levels over 1.0 mg/l. Even 1.0 mg/l is far higher than the EEC (7 ppb) so demonstrating that the LC₅₀ is higher than 1.0 mg/l was considered acceptable.

Registrant's Conclusions:

(Conclusions of Analytical BioChemistry Laboratories) LC₅₀ is greater than 300 mg/l (300 ppm)*.

*The EPA reviewer (R. Hitch) will ask that the registrant accept the LC₅₀ as being greater than 1 ppm as the pendimethalin came out of solution above this level.

Reference

Stephan, C. E., 1975. Methods for acute toxicity tests with fish, macroinvertebrates and amphibians. EPA-660/3-75-009.

104 Discussion

Propanil, as noted earlier in this review, is currently registered for rice use. Pendimethalin is of very low acute toxicity to terrestrial organisms. High quality acute fish pendimethalin studies have not been submitted to date but the tests that have been submitted indicate that the 96 hr. LC₅₀ might be around 1 ppm and that a warning statement regarding exposure to aquatic organisms would be necessary for this use pattern and in regard to disposal of unused pendimethalin.

The chronic toxicity of pendimethalin is a disputed issue at this point. A chronic study submitted by American Cyanamide showed statistically significant reductions in number of eggs, eggs per spawn, and eggs per female at 9.8 ppb when analyzed by EEB reviewer L. Windberg (see June 13, 1978 review).

Even if Mr. Windberg was correct, this would not trigger a concern as Joseph Reinert of the Environmental Fate Branch projects that pendimethalin concentrations should be in the range of about 7 ppb in waterways near rice fields which are flushed two days after the maximum application. On the other hand, chronic toxicity levels for aquatic invertebrates are often much lower than those for fish. The registrant is, therefore, asked in the conclusions to submit a life cycle study with Daphnia magna.

Further, the rice use pattern area lies within important wetland regions along the lower Mississippi River and the Texas-Louisiana Gulf coast (see figure 1). Catfish are harvested commercially in these areas and the acute exposure due to aerial drift of the prowl formulation would be an unreasonable hazard if the formulation proved to be acutely toxic to this and other important warmwater fish species. The registrant is therefore asked to submit acute toxicity information on the Prowl formulation.

Finally, because a very limited exposure to estuarine life is anticipated, tests with shrimp, oysters, and marine fish are required.

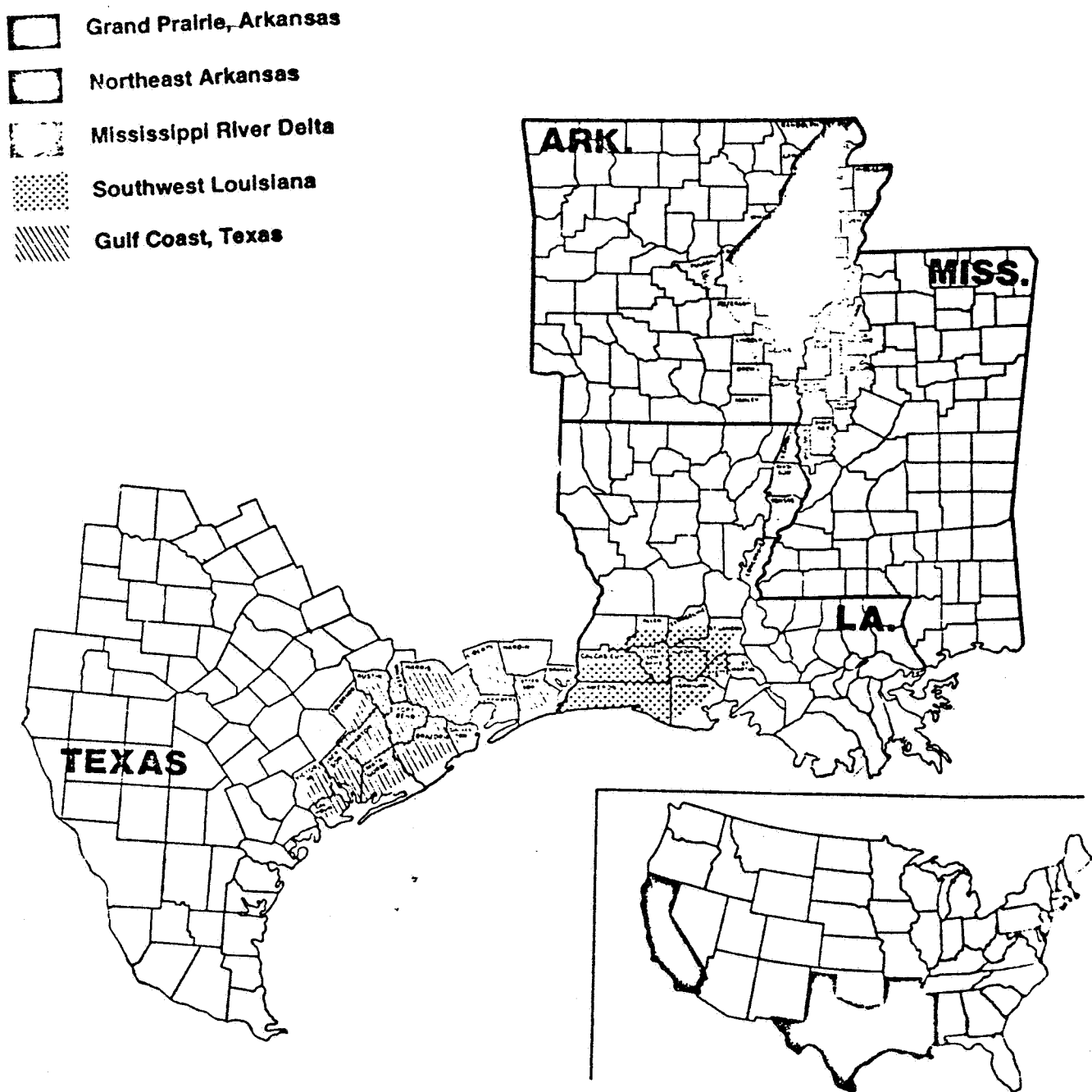


Figure 1. Major U.S. rice areas (adapted from Mullins et al. 1978).

Mullins, T., W. R. Grant, and S. H. Holder. 1978. U. S. Economics Statistics and Cooperatives Service, U. S. Dept. Agr. Stat. Bull. No. 613. Washington, D. C. 39 p.

Endangered Species Considerations

The only endangered or threatened species within the rice use pattern area which might, upon cursory consideration of projected exposure levels, be threatened by pendimethalin would be the fat pocketbook pearly mussel (Potameliopsis (= Proptera) capax). This species, however, lives in two large rivers - the White and St. Francis of Arkansas - which should provide great dilution during the early years of any pendimethalin use in rice. The registrant is asked to provide oyster larvae toxicity data but considering that the projected exposure in stagnant Bayous is only 7 ppb, it is unlikely that the oyster study will indicate a threat to a clam living in a flowing river.

Conclusions

EEB has reviewed the proposed conditional registration of Prowl for use on rice. EEB is unable to complete an incremental risk assessment (3(c)(7) finding) for this use because pertinent (ecological effects and/or environmental chemistry) data are lacking. In order to assess the risks associated with this use, EEB requires the following data:

1. An oyster larvae toxicity study conducted with the technical and formulated product.
2. A 96 hr. LC₅₀ study with a warmwater fish (preferably Ictalurus punctatus) conducted with the technical and formulated product.
3. An estuarine fish 96 hr. LC₅₀ study conducted with the technical and the formulated product.
4. A shrimp acute toxicity study conducted with the technical and the formulated product.
5. A chronic Daphnia study conducted with the technical chemical.

The crayfish toxicity study (ABC, Inc. study #25725; EPA Accession 099889) is judged satisfactory for supporting this registration for a rice use.

Robert K. Hitch

Robert K. Hitch
Fish and Wildlife Biologist

Date: 28/apr/81

(13)

David L. Coppage
David L. Coppage
Head Section #3 EEB

Date: 4/29/81

Clayton Bushong
Clayton Bushong

Date: 4/30/81

Note to PM:

The Ecological Effects Branch requests acute toxicity tests on warm water fish with formulations to support registrations in the southern rice growing states when aerial applications are intended. This information is pertinent as the southern rice fields adjoin many commercial and recreational fishing areas as well as fish nursery areas which might be affected by spray drift. Apparently, the Stam M-4 registration was not routed through EEB and the test with the formulation was not requested from the Stam M-4 registrant, Rohm and Haas. I will, therefore, have to request that Beltsville test this formulation. If you find my records are in error and that Rohm and Haas has submitted acute fish toxicity data please let me know as soon as possible so I will not have to request that Beltsville conduct the study.

Thanks.
Robert K. Hitch
557-5600