



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

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2-2-92

|| IN 22 1992

OFFICE OF
PESTICIDES AND TOXIC
SUBSTANCES

MEMORANDUM

SUBJECT: Response to the Propanil Reregistration
Standard: Residue Data (MRID #'s 42237101,
42237201 and 42237301, CBRS # 9589, Barcode No. D175886.)

FROM: R. B. Perfetti, Ph.D., Chemist
Reregistration Section
Chemistry Branch II: Reregistration Support
Health Effects Division (H7509C) *R B Perfetti*

THRU: E. Zager, Chief
Chemistry Branch II: Reregistration Support
Health Effects Division (H7509C) *E Zager*

TO: W. Burnam, Acting Chief
Science Analysis and Coordination Branch
Health Effects Division (H7509C)

and

L. Rossi, Chief
Reregistration Branch
Special Review and Reregistration Division (H7508C)

Attached is a review of propanil rice residue data submitted by the Propanil Task Force in response to the propanil Reregistration Standard. This information was reviewed by Acurex Corporation under supervision of CBRS, HED.

This document has undergone secondary review in CBRS and has been revised to reflect the Branch policies.

Please see our conclusions in the attachment regarding the adequacy of the information provided by the Registrant.

A Residue Chemistry Data Summary Table is also included at the end of this review.

If you need additional input please advise.

Attachment 1 : Review of Propanil Residue Data.

cc: With Attachment 1: R. B. Perfetti, Propanil Reregistration Standard File, Propanil Subject File, J. Burrell/C. Furlow (PIB/FOD), Acurex, Circ. (7).

cc: Without Attachment: RF.

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PROPANIL
(Chemical Code 028201)
(CBRS No. 9589; DP Barcode D175886)

TASK 3

**Registrant's Response
to Residue Chemistry Data
Requirements**

May 20, 1992

Contract No. 68-DO-0142

Submitted to:

U.S. Environmental Protection Agency
Arlington, VA 22202

Submitted by:

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PROPANIL

(Chemical Code 028201)

(CBRS No. 9589; DP Barcode D175886)

REGISTRANT'S RESPONSE TO RESIDUE CHEMISTRY REQUIREMENTS

Task 3

BACKGROUND

The Propanil Guidance Document dated 12/87 required data depicting the magnitude of residue in or on rough rice grain and straw from aerial and ground applications of propanil (3',4'-dichloropropionanilide) EC and SC/L formulations applied at 6 lb ai/A and harvested 56 days after treatment. The Guidance Document also requested data depicting residues in rice grain dust obtained from rough rice grain bearing measurable weathered residues.

In response to the Guidance Document, the Propanil Task Force submitted protocols for magnitude of residue studies on rice. These protocols were reviewed by H. Fonouni (CBRS No. 6442; 4/18/90) who noted that the maximum single and seasonal application rates for rice are 6 and 8 lb ai/A, respectively. The review also indicated that the registrant is only supporting aerial application(s) of the EC formulation for rice. The use of the SC/L formulation and ground application of the EC on rice are not being supported. The registrant subsequently submitted data (1992; MRIDs 42237101, 42237201, and 42237301) pertaining to the residues of propanil and its metabolites in or on rice grain and straw from aerial application(s) of the 4 lb ai/gal EC applied at the maximum labeled rates. These submissions also include an analytical method for determining propanil and its metabolites in rice and crayfish. These submissions are reviewed here to determine their adequacy in fulfilling outstanding magnitude of residue data requirements. The Conclusions and Recommendations stated in this review pertain only to magnitude of residue data for rice and analytical methodology for rice and crayfish.

The nature of the residue in plants is not adequately understood. The wheat metabolism study and additional data from the rice metabolism study remain outstanding.

Tolerances for residues of propanil in or on raw agricultural commodities are currently expressed in terms of propanil and its metabolites, calculated as propanil (40 CFR §180.274). Feed additive tolerances of 10 ppm are also established for propanil and its metabolites in rice bran, hulls, polishings, and mill fractions (40 CFR §186.1875).

The currently preferred enforcement method for plant and animal commodities is the GC method listed as Method I in PAM Vol II. The method employs base hydrolysis to convert propanil and its metabolites to DCA, which is then quantified.

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There is no established Codex MRL for residues of propanil or its metabolites in or on rice grain or straw. Therefore, there is no question with respect to Codex/U.S. tolerance compatibility.

CONCLUSIONS/RECOMMENDATIONS

- 1a. The submitted residue analytical GLC method, EN-CAS Method No. ENC-9/90, is adequate for depicting levels of propanil and its metabolites determined as base-released DCA in or on rice commodities and in crayfish.
- 1b. Recovery of DCA-glucose was adequate from fortified samples of crayfish using EN-CAS Method No. ENC-9/90. However, calculations pertaining to the recovery of DCA-glucose appear to contain errors. The registrant should clarify how the DCA-glucose recovery data were calculated.
- 2a. The data adequately depict the residues of propanil and its metabolites as base-released DCA in rice straw. The data indicate that residues are not likely to exceed the established tolerance of 75 ppm in or on rice straw harvested 60 days following aerial application(s) of propanil 4 lb ai/gal EC.
- 2b. The data adequately depict the residues of propanil and its metabolites as base-releasable DCA in rough rice grain. The data indicate that residues are likely to exceed the established tolerance of 2 ppm in or on rice grain harvested 60-97 days following aerial application(s) of the 4 lb ai/gal EC. Providing that TOX has no concerns, the registrant should purpose a revised tolerance for rice grain. However, outstanding data on the nature of the residue in rice should be submitted prior to submitting a petition for a revised tolerance.
3. Magnitude of residue data pertaining to the concentration of propanil residues in rice grain dust remain outstanding.
4. When new tolerances are purposed for rough rice grain, feed additive tolerances for processed fractions of rice grain must also be revised.

Note to SRRD: The tolerance for rice straw is currently listed as 75(N) ppm (40 CFR §180.274). The outdated designation "(N)", negligible, should be deleted from all 40 CFR entries.

DETAILED CONSIDERATIONS

Residue Analytical Methods

As part of the submitted rice data, the Propanil Task Force provided method validation data for EN-CAS Method No. ENC-9/90 for determination of propanil and its metabolites as base-released DCA in rice commodities and crayfish (Appendix I). This method is based on Method II in PAM, Vol. II, with substantial modifications.

In EN-CAS Method No. ENC-9/90, homogenized samples of rice commodities or crayfish are base hydrolyzed in boiling 5M NaOH for 16 hours and the hydrolysate product is steam distilled and partitioned into hexane using a Nielsen-Kryger distillation apparatus. The distilled hexane and aqueous fraction is frozen and separated. The aqueous phase is then thawed and reextracted with additional hexane. The hexane fractions are loaded onto a silica gel column and eluted using hexane:ethyl acetate (75:25, v/v). The eluant is analyzed for DCA by GC equipped with a fused capillary silica column (DB-17 or DB-1701) using a nitrogen-phosphorous detector. The limit of quantitation for the method is 0.01 ppm for crayfish, rough rice grain, polished rice grain, and rice straw, 0.05 ppm for rice hulls, and 0.02 ppm for rice bran.

For method validation, triplicate samples of rough rice grain, polished rice grain, rice straw, and crayfish tail meat were fortified with propanil at 0.01, 0.05 and 0.25 ppm. Rice hull samples were fortified with propanil at 0.05 and 0.25 ppm and rice bran samples were fortified at 0.02, 0.05, and 0.25 ppm. In addition, a second set of crayfish samples were fortified with DCA-glucose, a major crayfish metabolite, at 0.01, 0.05, and 0.25 ppm. Samples were analyzed by EN-CAS Method No. ENC-9/90 as described above. Sample chromatographs and calculation were also provided. Recoveries of propanil and DCA-glucose calculated from base-released DCA are presented in Table 1.

The data indicate that the method adequately recovers propanil as base-released DCA in rice commodities and crayfish. However, recoveries of DCA-glucose from crayfish as base-released DCA were low (54-66%) at the 0.05 and 0.25 fortification levels. It is noted that the low recoveries reported for the DCA-glucose fortifications may be the result of a calculation error. The registrant reported recovery data for DCA-glucose from crayfish in terms of propanil (mw = 218) rather than DCA-glucose (mw = 325). The conversion of base-released DCA to propanil equivalents rather than DCA-glucose equivalents would result in underestimating the mass equivalent recovered by a factor of 0.67. The registrant should clarify how the DCA-glucose recovery data were calculated.

Table 1. Recovery of propanil from fortified samples of crayfish, rice rough grain, polished grain, straw, hulls, and bran, and of DCA-glucose from fortified samples of crayfish, as determined by base hydrolysis to DCA.

Commodity	Fortification level (ppm)	Percent Recovery
Rough Rice Grain	0.01	80, 82, 84
	0.05	78, 90, 92
	0.25	70, 77, 85
Polished Rice Grain	0.01	113, 116, 119
	0.05	100, 119, 126
	0.25	78, 104
Rice Hulls	0.05	101, 113, 113
	0.25	80, 86, 90
Rice Bran	0.02	74, 91, 107
	0.05	60, 70, 94
	0.25	100, 108, 122
Rice Straw	0.01	93, 104, 138
	0.05	95, 96, 97
	0.25	63, 69, 72
Crayfish	0.01	65, 70, 90
	0.05	90, 93, 97
	0.25	88, 96, 99
Crayfish ^a	0.01	82, 85, 89
	0.05	66, 66, 66
	0.25	54, 57, 63

^aSamples fortified with DCA-Glucose.

Magnitude of the Residue in Plants.

Rices tolerances of 2 and 75 (N) ppm have been established for the residues of propanil and its metabolites, calculated as propanil, in or on rice grain and straw, respectively (40 CFR §180.274). Magnitude of residue protocols reviewed by the Agency (H. Fonouni; CBRS No. 6442; 4/18/90) indicate that the Propanil Task Force is currently supporting maximum single and seasonal application rates of 6 and 8 lb ai/A, respectively, with the maximum seasonal rate applied as two 4 lb ai/A applications. The registrant has also indicated that the only uses that will be supported for rice are the aerial application(s) of the 4 lb ai/gal EC formulations. The established PHI for rice is 56 days.

The Propanil Task Force submitted data (1991; MRIDs 42237101, 42237201, and 42237301) from 24 tests conducted in AR(6), CA(6), LA(6), and TX(6) depicting residues of propanil in or on rough rice grain and straw. Propanil (4 lb ai/gal EC) was applied aerially at either 4 lb ai/A, 6 lb ai/A, or twice at 4 lb ai/A. Applications were made at 10 gal/A. Each application rate was applied at two test sites in each state and each state had one test site that served as a control. The test sites ranged in size from 14-80 acres and were subdivided into three subplots, each containing three sampling areas from which samples were pooled. For the 4 and 6 lb ai/A application rates, propanil was applied at 18-49 days and 45-60 days after planting, respectively. For multiple applications, the first of the two 4 lb ai/A applications was applied at 18-31 days after planting and the second was applied within 14-17 days of the first, with the exception of one test site in AK that was retreated after 6 days.

Grain and straw samples were collected at maturity and immediately frozen. Posttreatment intervals ranged from 56-124 days, with only one test site being harvested at the established 56 day PHI. Samples were held in frozen (<20 °C) storage for 8 to 11 months prior to extraction and analysis. The Propanil Reregistration Standard (8/87) previously concluded that residues of propanil are stable in frozen rice grain for up to 17 months and in rice straw at room temperature for up to 8 months.

Samples of rough rice grain and straw were analyzed using EN-CAS Method No. EN-9/90, a GLC method described above that determines propanil residues as base-released DCA. The detection limit for rough grain and straw is 0.01 ppm. Three separate samples were analyzed from each test site, with the exception of the control site from LA at which samples from the entire test site were pooled into a single sample. Residues of propanil were detected in control samples of grain and straw from LA and TX and in straw from AR (Table 2). Control samples of grain and straw from CA were fortified with DCA at 0.01-10 ppm and at 0.01-2 ppm, respectively, to determine method recoveries. Method recoveries of DCA from grain and straw ranged from 61-109% and 65-101%, respectively. Residues of propanil in or on rough rice grain and straw determined as base-released DCA and expressed as propanil equivalents are presented in Table 2.

Table 2. Residues of propanil and its metabolites determined as base-released 3,4-dichloroaniline in or on rice grain and straw following aerial application(s) of propanil as a 4 lb ai/gal EC.

Matrix	Rate ^a	State	Posttreatment Interval (days) ^b	# of samples	Residues (ppm) ^c
Rice grain	Control	AR	NA ^d	3	<0.01
		CA	NA	3	<0.01
		LA	NA	1	0.07
		TX	NA	3	0.04 - 0.12
Rice grain	4 lb ai/A	AR	108-109	6	0.01 - 0.03
		CA	118-124	6	0.01 - 0.11
		LA	98-111	6	0.01 - 0.04
		TX	89-91	6	0.01 - 0.15
Rice grain	6 lb ai/A	AR	109-111	6	0.04 - 0.11
		CA	72-97	6	0.73 - 2.43
		LA	56-68	6	0.39 - 1.49
		TX	60-61	6	2.03 - 9.18
Rice grain	4+4 lb ai/A	AR	95-105	6	0.03 - 0.04
		CA	103-116	6	0.12 - 0.46
		LA	80-83	6	0.09 - 0.34
		TX	64	6	2.2 - 2.7
Rice straw	Control	AR	NA	3	0.01 - 0.03
		CA	NA	3	<0.01
		LA	NA	1	0.07
		TX	NA	3	0.22 - 0.80
Rice straw	4 lb ai/A	AR	108-109	6	0.07 - 0.14
		CA	118-124	6	0.05 - 0.16
		LA	98-111	6	0.11 - 0.22
		TX	89-91	6	0.23 - 0.49
Rice straw	6 lb ai/A	AR	109-111	6	0.03 - 0.14
		CA	72-97	6	8.6 - 28.4
		LA	56-68	6	1.6 - 13.5
		TX	60-61	6	9.6 - 40.5
Rice straw	4+4 lb ai/A	AR	95-105	6	0.09 - 0.18
		CA	103-116	6	1.6 - 6.8
		LA	80-83	6	0.41 - 4.2
		TX	64	6	4.5 - 10.4

^aApplied in 10 gal/A.

^bThe posttreatment interval for the 4 + 4 lb ai/A application rate was based on the date of the second application.

^cCalculated as ppm equivalents of propanil.

^dNot applicable.

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Geographic representation is adequate. The states of AR(41%), CA(21%), LA(14%), and TX(12%) accounted for 88% of the 1989 rice production in the United States (Agricultural Statistics, 1990, p. 22).

The data adequately support the established tolerance for propanil and its metabolites in or on rice straw. The highest level of residues measured were from the 6 lb ai/A application rate harvested at 60 days posttreatment, which closely approximates the current PHI of 56.

The data do not adequately support the established tolerance for propanil and its metabolites in or on rice grain. Data from the TX test sites indicate that residues are likely to exceed the established tolerance of 2 ppm for rice grain from aerial applications at the maximum single application rate (6 lb ai/A) or the maximum seasonal application rate (8 lb ai/A). All grain samples from TX at these application rates had residues in excess of 2 ppm. The highest level measured was 9.18 ppm. The posttreatment interval for the TX grain samples closely approximated the 56 day PHI established for rice. In CA, residues also exceeded the established tolerance in or on rice grain treated at 6 lb ai/A and harvested at up to 97 days posttreatment. Of the six CA grain samples analyzed from this treatment, four had residues > 2 ppm.

Providing that TOX has no concerns, the registrant should propose a revised tolerance for rice grain. The data indicate that 10 ppm is an appropriate tolerance for rough rice grain harvested at 60 days posttreatment. However, outstanding data on the nature of the residue in rice should be submitted prior to submitting a petition for new or revised tolerances. In addition, when higher tolerances are proposed for rice grain, feed additive tolerances for rice bran, hulls, polishings, and mill fractions will also have to be revised. The Propanil Reregistration Standard previously concluded that residues of propanil concentrate in rice hulls by 5x and in rice bran by 13x. Before revisions are proposed to the current feed additive tolerances, the registrant should submit the outstanding data depicting residues of propanil in rice grain dust processed from grain bearing measurable weathered residues.

The data do not support the currently labeled PHI of 56 days as residues in rice grain harvested up to 97 days posttreatment exceeded the tolerance. Given the variation in posttreatment harvest intervals in the current studies, insufficient data are available for determining an appropriate PHI. However, the residue data from TX support a PHI of 60 days if the tolerance is revised to 10 ppm for rice grain.

References

Citations for the MRID documents referenced in this review are presented below. Submissions reviewed in this document are indicated by shaded type.

42237101 Young, D.; Palmer, D.; Johnson, G.; et al. (1992) Magnitude of the Residues of Propanil in or on Rough Rice Grain Treated with Propanil 4 EC at 6 lb ai/Acre: Lab Project Number: 271-107. Unpublished study prepared by Wildlife International Ltd. and EN-CAS Analytical Labs. 430 p.

42237201 Young, D.; Palmer, D.; Johnson, G.; et al. (1992) Magnitude of the Residues of Propanil in or on Rough Rice Grain Treated with Propanil 4 EC at 4 lb ai/Acre: Lab Project Number: 271-105. Unpublished study prepared by Wildlife International Ltd. and EN-CAS Analytical Labs. 438 p.

42237301 Young, D.; Palmer, D.; Johnson, G.; et al. (1992) Magnitude of the Residues of Propanil in or on Rough Rice Grain Treated with Propanil 4 EC at 4 lb + 4 lb ai/Acre: Lab Project Number: 271-106. Unpublished study prepared by Wildlife International Ltd. and EN-CAS Analytical Labs. 444 p.

Agency Memoranda:

CBRS No. 6442
Subject: Propanil Registration Standard - Magnitude of the Residue in/on Rice, Processed Products of Rice, Irrigation water and Crayfish: Field Study Protocols.
From: H. Fonouni
To: B. Baker and R. Engler
Dated 4/18/90
MRID(s) N/A

PROPANIL (CASE No. 226)
TENTATIVE RESIDUE CHEMISTRY DATA SUMMARY THROUGH 6/22/92¹
REASSESSMENT OF U.S. TOLERANCES AND POTENTIAL FOR HARMONIZATION WITH CODEX²

Guideline Number and Topic ³	Are data requirements satisfied?	MRID(s) ⁴
171-3 Directions for use		
171-4(a) Plant Metabolism	N ^{5,6}	42209200,42209201
171-4(b) Animal Metabolism	N ^{7,8}	41755001,41755301 41848801,41983901
171-4(c) Residue Analytical Methods - Plants	N	
171-4(d) Residue Analytical Methods - Animals	N	
171-4(e) Storage Stability	N	
171-4(k) Crop Field Trials		
171-4(k) Cereal Grains Group		
Barley [see 171-4(l)]	N	
Oats [see 171-4(l)]	N	
Rice [see 171-4(l)]	Y ⁹	42237101, 42237201
Wheat [see 171-4(l)]	N	
171-4(k) Forage, Fodder, and Straw of Cereal Grains		
Barley forage and straw	N	
Oats forage and straw	N	
Rice straw	Y ¹⁰	42237301
Wheat forage and straw		
171-4(l) Processed Food/Feed		
Rice	N	
Wheat	N	
171-4(j) Meat/Milk/Poultry/Eggs	N	
171-4(f) Potable Water	N	
171-4(g) Fish	N ¹¹	41448901, 41849101
171-4(h) Irrigated Crops	N	
171-4(i) Food Handling Establishments	N/A	
171-5 Reduction of Residues	N/A	

¹Registration Standard issued 12/87. No Reregistration Standard Update issued.

² There are no Codex MRL's proposed or established for propanil.

³N/A = Guideline requirement not applicable.

⁴MRIDs that were reviewed in the current submission are designated in shaded type.

⁵ CBRS# 8703, 2/14/92 (C. Olinger): Interim rice metabolism report. Additional information is needed.

⁶CBRS 9528, 4/2/92 (J. Abbotts): Wheat metabolism study. Additional information is needed. Only parent is characterized, representing no more than 13% of the TRR.

⁷ CBRS# 7622, 2/21/92 (C. Olinger): Metabolism in poultry is adequately understood. Additional information on the methodology, a lab validation and a method trial are needed.

⁸ CBRS#'s 7960 and 8522, 3/18/92 (R. Perfetti): Additional information regarding radioactive residues milk and fat are needed in order to upgrade this study.

⁹CBRS # 9589, R. Perfetti, 6/22/92; The data for rice grain is acceptable. However a higher tolerance is needed. Ten ppm would be adequate. When the higher tolerance is established for rice grain, then the food/feed additive tolerances for processed fractions must also be revised.

¹⁰CBRS # 9589, R. Perfetti, 6/22/92; Residue data on rice straw indicate that the established tolerance is adequate. No additional data on straw is needed.

¹¹ CBRS#'s 7960 and 8522, 3/18/92 (R. Perfetti): The metabolism of propanil in crayfish is adequately understood. Magnitude of the residue data in fish and shellfish are required.

cc: RBP; Propanil Reregistration Standard File; L. Rossi, SRRD.

