Kereg. Std file 9/2/92

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

SEP - 2 1992

OFFICE OF
PESTICIDES AND TOXIC
SUBSTANCES

MEMORANDUM

SUBJECT: Response to the Propanil Reregistration Standard: Residue Chemistry (MRID #'s 42200401 and 42200501, CBRS # 9541, Barcode: D175417).

FROM: R. B. Perfetti Ph.D., Chemist
Reregistration Section 1
Chemistry Branch II: Reregistration Support
Health Effects Division (H7509C)

THRU: P. Deschamp, Acting Section Head
Reregistration Section 1
Chemistry Branch II: Reregistration Support
Health Effects Division (H7509C)

TO: Lois Rossi, Chief
Reregistration Branch
Special Review & Reregistration Division (H7508W)

and

E. Saito, Acting Chief
Chemical Coordination Branch
Health Effects Division (H7509C)

Attached is a review of residue chemistry data submitted in response to the propanil Reregistration Standard. This review was completed by Acurex Corporation under supervision of CBRS, HED. It has undergone secondary review in the branch and has been revised to reflect Agency policies.

A revised Tentative Residue Chemistry Summary sheet is included.

If you need additional input please advise.

Attachment 1: Propanil Residue Chemistry Data Review.

cc (With Attachment 1): RBP, Propanil Reregistration Standard File, Propanil Subject File, RF, Circ. and Acurex.

PROPANIL
(Chemical Code 028201)
(CBRS No. 9541; DP Barcode D175417)

TASK 3

Registrant's Response to Residue Chemistry Data Requirements

July 2, 1992

Contract No. 68-DO-0142

Submitted to:

U.S. Environmental Protection Agency
Arlington, VA 22202

Submitted by:

Acurex Environmental Corporation
Eastern Region Operations
4915 Prospectus Drive
P.O. Box 13109
Research Triangle Park, NC 27709

2

PROPANIL

(Chemical Code 028201)

(CBRS No. 9541; DP Barcode D175417)

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 irrigation and potable water resulting from application to rice. In response, the Propanil Task Force discussed these data requirement with the Agency and they were advised that careful monitoring of paddy water in conjunction with the aquatic field dissipation study would suffice for this requirement (letter from R. Novak, Technical Director, Propanil Task Force, to R. Perfetti, dated 11/6/89). Subsequently, the Task Force submitted a protocol that was reviewed by the Agency (CBRS No. 6442; H. Fonouni, dated 4/18/90). The Agency review accepted the Task Force's proposal to treat aerially two fields in AR and LA using the 4 lb/gal EC formulation 30 days after planting the rice and to collect water samples at depths of <0.5 m. In addition, the review stipulated that two applications should be made at 4 lb ai/A each, and that the label should specify a minimum interval between applications. The review also noted that all uses of propanil on rice except aerial application of the EC formulation should be canceled, as the other uses were not to be supported by residue data.

The Propanil Task Force has submitted data from the rice paddy study to fulfill the requirements for aquatic field dissipation and irrigation/potable water data (1992; MRIDs 42200401 and 42200501). These data are reviewed here for adequacy in fulfilling residue chemistry data requirements. The Conclusions and Recommendations stated herein pertain only to irrigation water/potable water data requirements. The adequacy of these studies to satisfy requirements for aquatic field dissipation will be addressed by EFGWB/EFED.

According to the current submission, 3,4-dichloroaniline (3,4-DCA) was "the only significant [propanil] metabolite found in an aquatic metabolism study." Residues of propanil in irrigation and potable water are not currently regulated by the EPA.

CONCLUSIONS

1. The data indicate that propanil and 3,4-DCA (extractable and base-releasable) decline to nondetectable levels (<0.01 ppm) in rice paddy and discharge water 60 days after registered propanil application.

2. The product label(s) currently do not specify a minimum interval between applications. The data indicate that a 14-day interval would be appropriate. In addition, the current label directions for ground equipment should be deleted, as ground applications have not been supported by residue data.

RECOMMENDATIONS

Propanil product labels bearing use directions for rice should be amended to prohibit the discharge of rice paddy water within 60 days of the last application. This will obviate the need for an MCL in water and for tolerances in irrigated crops. The current half-mile restriction on discharging water in the vicinity of a potable water intake from flowing or standing water should remain on the label(s). In addition, the label(s) should be amended to specify a minimum interval between repeat applications and to remove the directions for ground application.

DETAILED CONSIDERATIONS

Residue Analytical Methods

The Propanil Task Force (1992; MRIDs 42200401 and 42200501) submitted data pertaining to solvent extractable propanil and 3,4-DCA and base hydrolyzable 3,4-DCA to satisfy irrigation and drinking water requirements for residue chemistry. These data were collected using EN-CAS Laboratories methods ENC-5/90 for soluble propanil and 3,4-DCA and ENC-9/90 for base-released residues.

In method ENC-5/90, phosphate buffer at pH 6.5 is added to the water sample, which is then passed through a methanol/water-preconditioned C18 Mega Bond Elut cartridge. Residues are eluted with ethyl acetate and analyzed by capillary column GC with an alkali flame (N/P) detector. The retention times are 11.8 minutes for propanil and 6.5 minutes for 3,4-DCA. The detection limit is 0.01 ppm for each compound. Recovery data are reported in Table 1. Procedural recoveries obtained concurrently with residue samples are presented below in the "Magnitude of the Residue" section.

Table 1. Recoveries of propanil and 3,4-DCA from water, fortified with each compound and analyzed using method ENC-5/90.

Fortification (ppm)	Propanil	3,4-DCA
	----------% Recovery[a]----------	
0.01	62-107 (77)	89-105 (96)
0.1	70-109 (93)	83-108 (98.9)
1.0	67-91 (80.5)	84-103 (92.2)

[a]Values in parentheses are the means of 14 samples in each range.

4

Method ENC-9/90 is similar to Method I in PAM, Vol. II in terms of hydrolysis and extraction. 3,4-DCA-containing residues are simultaneously hydrolyzed and extracted by boiling the water sample in 5 N sodium hydroxide and hexane for 6 hours. The aqueous and hexane phases are separated and the aqueous fraction is re-extracted with hexane. The base-released 3,4-DCA residues in hexane are passed through hexane-preconditioned silica gel and eluted with hexane:ethyl acetate (75:25, v/v). 3,4-DCA residues are analyzed by GC as described above for method ENC-5/90. The detection limit is 0.01 ppm. Recovery data are reported in Table 2. Procedural recoveries obtained concurrently with residue samples are presented below in the "Magnitude of the Residue" section.

Table 2. Recovery of 3,4-DCA from fortified water samples using the base hydrolysis method, ENC-9/90.

Fortification (ppm)	Recovery (%)[a]
0.01	66-127 (94.8)
0.1	60-93 (85.6)
1.0	61-80 (74.3)

[a]Mean values for 13 or 14 samples in each range given in parentheses.

These methods are adequate for data collection pertaining to residues of propanil and 3,4-DCA and base-hydrolyzable 3,4-DCA in water.

Storage Stability Data

The Propanil Task Force (1992; MRIDs 42200401 and 42200501) submitted storage stability data to support the residue data on rice paddy water. Samples from the test paddy in LA were collected prior to treatment and were fortified with propanil or 3,4-DCA. Samples from an untreated paddy in AR were used for field fortifications. The report stated that untreated ambient-temperature water samples were collected, fortified, and stored in a chest type freezer at the test sites. Untreated water samples collected as just described were fortified in the laboratory as well, for stability determinations. Samples were analyzed for extractable propanil and 3,4-DCA following various storage intervals. The results are summarized in Tables 3 through 6; it should be noted that the data presented have not been corrected for method recovery.

5

Table 3. Storage stability of propanil and 3,4-DCA in water samples fortified at 0.1 ppm in the field (Arkansas study, MRID 42200401).

Storage Interval (weeks)	Extractable		
	Propanil	3,4-DCA	Base-released 3,4-DCA
	% Recovery[a]		
17	88, 76	72, 74	90, 89
	(88, 109)	(92, 90)	(119, 115)
39	82, 76	57, 56	54, 55
	(89, 93)	(96, 104)	(77, 91)

[a]Values are not corrected for method recovery; concurrent method recoveries from fresh fortifications are given in parentheses.

Table 4. Storage stability of propanil and 3,4-DCA in water samples fortified at 0.1 ppm in the laboratory (Arkansas study, MRID 42200401).

Storage Interval (weeks)	Extractable		
	Propanil	3,4-DCA	Base-released 3,4-DCA
	% Recovery[a]		
0	91, 101	87, 90	95, 86
	(82, 92)	(95, 80)	(94, 90)
4	97, 88	92, 93	--
	(83, 81)	(85, 93)	--
10	--	--	82, 77
	--	--	(101, 91)
16	80, 55	89, 98	83, 89
	(87, 88)	(97, 107)	(96, 97)
36	73, 51	85, 76	103, 68
	(103, 95)	(105, 96)	(114, 107)
51	71, 81	117, 110	92, 100
	(115, 118)	(120, 128)	(103, 112)

[a]Data are not corrected for method recovery; concurrent method recoveries from freshly fortified samples are given in parentheses.

6

Table 5. Storage stability of propanil and 3,4-DCA in water samples fortified at 0.1 ppm in the field (Louisiana study, MRID 42200501).

Storage Interval (weeks)	Extractable		
	Propanil	3,4-DCA	Base-released 3,4-DCA
	% Recovery[a]		
18-20	82, 100	37, 43, 33, 48	79, 73
	(93, 94)	(85, 88, 87, 86)	(100, 81)
34/35	76, 86	147, 128	74, 70
	(105, 90)	(126, 136)	(102, 107)

[a]Values are not corrected for method recovery; concurrent method recoveries from fresh fortifications are given in parentheses.

Table 6. Storage stability of propanil and 3,4-DCA in water samples fortified at 0.1 ppm in the laboratory (Louisiana study, MRID 42200501).

Storage Interval (weeks)	Extractable		
	Propanil	3,4-DCA	Base-released 3,4-DCA
	% Recovery[a]		
0	96, 95	76, 78	95, 86
	(98, 94)	(72, 78)	(105, 92)
5	76, 104	90, 96	--
	(104, 121)	(83, 83)	--
12/13	102, 85	58, 65	49, 51
	(86, 103)	(103, 104)	(110, 95)
15	--	110, 111	--
	--	(130, 120)	--
17	96, 85	103, 87	45, 52
	(90, 83)	(91, 96)	(95, 92)
35/36	111, 102	48, 62	73, 79
	(91, 99)	(100, 98)	(73, 68)
53/54	124, 107	82, 83, 57, 83, 95, 58	113, 118, 106, 119, 114, 104
	(103, 107)	(98, 91)	(118, 108)

[a]Data are not corrected for method recovery; concurrent method recoveries from freshly fortified samples are given in parentheses.

These data adequately represent the storage intervals of the treated samples (up to about 32 weeks). Recoveries from field and laboratory fortified samples were variable, with the AR

7

field-fortified samples showing a decline in soluble and base-releasable 3,4-DCA of approximately 40% after 39 weeks in storage (Table 3). The registrant explained that the field samples were at ambient temperature and were likely biologically active. This factor, together with the large thermal mass of the samples (40 L) which precluded rapid freezing, could have been responsible for the observed decline. However, CBRS concludes that residue decline during storage does not present a problem for evaluating the residue data. The half-lives of extractable and base-released 3,4-DCA in the AR study were short, 3.12 and 7.16 days respectively. Thus, actual residues below the detection limit, if any, would be very low in 30- and 60-day samples and would not be expected to exceed 0.01 ppm if corrected for 40% storage loss.

Magnitude of the Residue in Irrigation and Drinking Water

The 4 lb/gal EC formulation (EPA Reg. No. 707-109) is registered for ground and aerial application to rice at 3-6 lb ai/A/application, not to exceed 8 lb ai/A/season. Aerial applications are made in a minimum of 10 gal/A and ground applications are to be made in 15 gal/A. There is no minimum interval between applications specified. The label carries the following restriction: "Water from treated rice fields must not be used to irrigate other crops or released within one half mile upstream of a potable water intake in flowing water (i.e., river, stream, etc.) or within one half mile of a potable water intake in a standing body of water such as a lake, pond, or reservoir."

The Propanil Task Force (1992; MRIDs 42200401 and 42200501) submitted data from two tests conducted in AR and LA depicting propanil and 3,4-DCA residues in paddy water and discharge water from rice paddies treated aerially with propanil. Two applications of the 4 lb/gal EC formulation were made at 4 lb ai/A/application (1x the maximum seasonal rate) in 10 gal/A. In the AR test, the first application was made to the drained field 22 days after planting and the second application was made 6 days later; the field was flooded within 24 hours of the second application. In the LA test, the field was flooded after the seedlings were established, drained prior to each propanil application, and re-flooded beginning within 24 hours of each application; these treatments were made 43 days after planting and again 14 days later.

At each site, 20 sampling stations were established along each of three transects and on each sampling day one station was selected randomly. Paddy water samples were collected within the upper 0.5 m of water on the day of the second application and at intervals up to 60 days thereafter. Discharge water was collected from the low point of each paddy on days 7, 14, and 60 after the second treatment.

Residue data on solvent-extractable propanil and 3,4-DCA and on base-releasable 3,4-DCA in the collected water samples were collected using methods ENC-5/90 and ENC-9/90, respectively. The detection limits were 0.01 ppm for each compound. Recoveries were (i) extractable propanil: 76-126% and 98-113%, respectively, from samples fortified at 0.01 and

9

1 ppm; (ii) extractable 3,4-DCA: 60-131% and 92-121%, respectively, from samples fortified at 0.01 and 1 ppm; and (iii) base-released 3,4-DCA: 90-127% and 65-98%, respectively, from samples fortified at 0.01 and 1 ppm (each range represents 13 or 14 samples). These methods are adequate for data collection. The results are summarized in Tables 7, 8, and 9.

Table 7. Residues in rice paddy water and discharge water following a single application of propanil (Arkansas study, MRID 42200401).

PTI (days)[a]	# Samples	Extractable		Base-released
		Propanil	3,4-DCA	3,4-DCA
Paddy water		----------Residues (ppm)----------		
1	1	<0.01	0.17	0.22
2	1	<0.01	1.5	0.98
3	2	<0.01	<0.01, 0.06 (0.04)	<0.01, 0.07 (0.04)
5	2	<0.01	0.13, 0.04 (0.08)	0.24, 0.05 (0.15)
7	3	<0.01	<0.01-0.06, (0.03)	0.09, 0.17, 0.02 (0.09)
14	2	<0.01	<0.01	0.03, 0.07 (0.05)
21	3	<0.01	<0.01	<0.01-0.07 (0.03)
30	3	<0.01	<0.01	0.01, <0.01 (0.01)
60	3	--	--	<0.01, 0.01 (0.01)
Discharge Water		----------Residues (ppm)----------		
7	1	<0.01	0.09	0.17
14	1	<0.01	<0.01	0.07
21	1	<0.01	<0.01	<0.01
60	1	--	--	<0.01

[a]Days after application to drained field; field flooded beginning within 24 hours of application.

Table 8. Residues in rice paddy water following application of propanil (Louisiana study, MRID 42200501).

PTI (days)[a]	Extractable		Base-released 3,4-DCA
	Propanil	3,4-DCA	
	Residues (ppm)[b]		
T1+0[c]	2.1	0.51	2.3
T1+6	<0.01	<0.01-0.08 (0.04)	0.01-0.14 (0.07)
T1+12	<0.01	<0.01-0.01	0.03-0.09 (0.07)
T2-1	<0.01	<0.01	0.05
T2+0[c]	0.64-2.3 (1.6)	0.11-0.5 (0.24)	0.72-2.4 (1.5)
T2+1	<0.01	0.21-0.7 (0.38)	0.36-0.85 (0.55)
T2+2	<0.01	0.1-0.41 (0.22)	0.18-0.59 (0.34)
T2+3	<0.01	0.09-0.14 (0.12)	0.18-0.32 (0.25)
T2+5	<0.01	0.01-0.07 (0.04)	0.03-0.18 (0.13)
T2+7	<0.01	0.03-0.04 (0.03)	0.08-0.25 (0.16)
T2+14	<0.01	<0.01	0.04-0.09 (0.06)
T2+21	<0.01	<0.01	0.03-0.08 (0.06)
T2+30	<0.01	<0.01	<0.01-0.03 (0.02)
T2+60	--	--	<0.01-0.01 (0.01)

[a]PTI = post-treatment interval; codes indicate days before (-) or after (+) the first treatment (T1) or second (T2). [b]Three samples collected and analyzed, except at T1+0, when only one transect was sampled; mean values given in parentheses. [c]Sample taken after treatment to drained paddy; whether or not re-flooding had begun was not reported.

Table 9. Residues in discharge water from a rice paddy in Louisiana following treatments with propanil (MRID 42200501).

PTI (days)[a]	Extractable		Base released 3,4-DCA
	Propanil	3,4-DCA	
	Residues (ppm)[b]		
T1-1	<0.01	<0.01	<0.01
T1+0[c]	2.8-5.3 (4.1)	0.17, 0.43 (0.3)	2.7, 3.9 (3.3)
T1+6	<0.01	0.03, 0.07 (0.05)	0.06, 0.15 (0.11)
T1+12	<0.01	<0.01	0.08, 0.03 (0.06)
T2-1	<0.01	<0.01	0.03, 0.06 (0.05)
T2+0[c]	0.7-1.0 (0.85)	0.09, 0.05 (0.07)	0.88, 0.63 (0.76)
T2+1	<0.01	0.17, 0.68 (0.43)	0.34, 0.86 (0.60)
T2+2	<0.01	0.11, 0.14 (0.13)	0.09, 0.22 (0.16)
T2+3	<0.01	0.08, 0.24 (0.16)	0.37, 0.19 (0.28)
T2+5	<0.01	0.04, 0.08 (0.06)	0.16, 0.13 (0.15)
T2+7	<0.01	0.01, 0.03 (0.02)	0.09, 0.12 (0.11)
T2+14	<0.01	<0.01	0.05, 0.06 (0.06)
T2+21	<0.01	<0.01	0.04, 0.05 (0.05)
T2+30	<0.01	<0.01	0.04, 0.02 (0.03)
T2+60	--	--	<0.01

[a]PTI = post-treatment interval; codes indicate days before (-) or after (+) the first treatment (T1) or second (T2). [b]Three samples collected and analyzed, except at T1+0, when only one transect was sampled; mean values given in parentheses. [c]Sample taken after treatment to drained paddy; whether or not re-flooding had begun was not reported.

The highest residue levels were observed in the discharge water from the Louisiana site on the same day of the first application (T1+0 samples; Table 9). Applications were made to drained fields and re-flooding was begun within 24 hours. The registrant did not report whether or not re-flooding had been started when the T1+0 samples were collected.

The data indicate that residues of propanil and extractable and base-releasable 3,4-DCA decline to nondetectable levels (<0.01 ppm) 60 days after application. Propanil product labels bearing use directions for rice should be amended to prohibit the discharge of rice paddy water within 60 days of the last application. This will obviate the need for an MCL in water and for tolerances in irrigated crops. The current half-mile restriction on discharging water in the vicinity of a potable water intake from flowing or standing water should remain on the label(s). The label(s) should also be amended to specify a minimum interval between repeat applications and to delete directions for ground applications.

References

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

42200401 Young, D.; Palmer, D.; Johnson, G.; et al. (1992) Aquatic Field Dissipation and Irrigation Water Residues of Propanil Following Application of Propanil 4 EC to an Arkansas Rice Paddy: Lab Project Number: 90-0019. Unpublished study prepared by Wildlife International Ltd. 666 p.

42200501 Young, D.; Palmer, D.; Johnson, G.; et al. (1992) Aquatic Field Dissipation and Irrigation Water Residues of Propanil Following Application of Propanil 4 EC to a Louisiana Rice Paddy: Lab Project Number: 90-0019. Unpublished study prepared by Wildlife International Ltd., and EN-CAS Analytical Labs. 682 p.

Agency Memoranda

CB No.: N/A
Subject: Propanil Registration Standard, RS-0226.
To: R. Perfetti
From: R.A. Novak
Dated: 11/6/89
MRID(s): N/A

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, dated 2/12/90.
To: B. Baker
From: H. Fonouni
Dated: 4/18/90
MRID(s): N/A

PROPANIL (CASE No. 226)
TENTATIVE RESIDUE CHEMISTRY DATA SUMMARY THROUGH 8/28/92[1]
REASSESSMENT OF U.S. TOLERANCES AND POTENTIAL FOR HARMONIZATION WITH CODEX[2]

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	Y [11]	42200401,42200501
171-4(g) Fish	N[12]	41448901, 41849101
171-4(h) Irrigated Crops	Y	
171-4(i) Food Handling Establishments	N/A	
171-5 Reduction of Residues	N/A	

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

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

[3]N/A = Guideline requirement not applicable.

[4]MRIDs 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.

[6]CBRS 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.

[9]CBRS # 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.

[10]CBRS # 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 #9541, RBP (8/28/92). Provided the Registrant amends the propanil label to prohibit the discharge of rice paddy water within 60 days of the last application there is no need for an MCL for propanil residues in water or for tolerances in irrigated crops. A 14 day interval between applications should be specified on the label. The current label directions for ground applications should be deleted.

[12] 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.