

Chemical Code: **028201**

Date Out: **AUG 26 1993**

ENVIRONMENTAL FATE AND GROUND WATER BRANCH

Review Action

To: **W. Waldrop/E. Feris**
Product Manager 71, Reregistration Division (H7508W)

From: **Akiva Abramovitch, Section Head, Environmental Fate Review Section #3**
Environmental Fate and Ground Water Branch
Environmental Fate and Effects Division (H7507C) ✱

Thru: **Hank Jacoby, Chief, Environmental Fate and Ground Water Branch**
Environmental Fate and Effects Division (H7507C)

Henry Jacoby
8/26/93

Attached, please find the EFGWB review of...

DPBarcode:	D170393, D174696, D183248, <u>D192580</u> , <u>D192651</u>		
Common Name:	Propanil	Trade name:	
Company Name:	various acting as the Propanil Task Force		
ID #:			
Purpose:	submission of data on soil photolysis, leaching/adsorption/desorption, aquatic field dissipation and run-off; response to reviews on aerobic soil metabolism, aqueous photolysis, aerobic and anaerobic aquatic metabolism		

Type Product:	Action Code:	EFGWB #(s):	Review Time:
herbicide	various	92-0122, 92-0517, 93-0023, 93-0834, 93-0855	

STATUS OF STUDIES IN THIS PACKAGE:

Guideline #	MRID	Status ¹
161-1	00111395	
162-1	*	A
162-2,3,4	*	A
163-1	427804-01	C

STATUS OF DATA REQUIREMENTS:

Guideline #	MRID#	Status ²
161-1	00111395	S
161-2	410707-01	S
165-4	none	W

¹Study Status Codes:

A=Acceptable U=Upgradeable C=Ancillary I=Invalid.

²Data Requirement Status Codes: S=Satisfied P=Partially satisfied N=Not satisfied R=Reserved W=Waived

* This submission contains the response to reviews of studies previously received. MRID# 415387-01 for aerobic soil metabolism; MRID# 418726-01 for anaerobic soil and anaerobic and aerobic aquatic metabolism.

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Hank Jacoby
8/26/93

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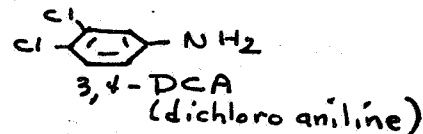
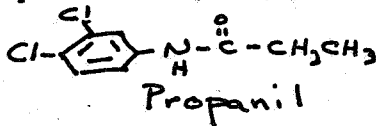
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1. CHEMICAL:

chemical name: 3,4-dichloropropionanilide, N-(3,4-dichlorophenyl) propanamide
common name: Propanil
trade name: n.a.
structure:
CAS #: 709-98-8
Shaughnessy #: 28201



2. TEST MATERIAL: n.a.

3. STUDY/ACTION TYPE:

4. STUDY IDENTIFICATION:

EFGWB 92-0122, DP barcode D170393 -- response to EFGWB review of aerobic soil metabolism study

EFGWB 92-0517, DP barcode D174696 -- aquatic field dissipation and irrigation water studies -- DATA INCLUDED

Young, D.P., Jr., Palmer, D.A., Johnson, G.D., Krueger, H., Hutchinson, C. Aquatic Field Dissipation and Irrigation Water Residues of Propanil following Application of Propanil 4 EC to an Arkansas Rice Paddy. performed by Wildlife International Ltd., Easton, MD, and EN-CAS Analytical Laboratories, Winston-Salem, NC. received at EPA 2/12/92 under MRID# 422004-01

Young, D.P., Jr., Palmer, D.A., Johnson, G.D., Krueger, H., Hutchinson, C. Aquatic Field Dissipation and Irrigation Water Residues of Propanil following Application of Propanil 4 EC to an Louisiana Rice Paddy. performed by Wildlife International Ltd., Easton, MD, and EN-CAS Analytical Laboratories, Winston-Salem, NC. received at EPA 2/12/92 under MRID# 422005-01

EFGWB 93-0023, DP barcode D183248 -- response to EFGWB review of aqueous photolysis, anaerobic and aerobic aquatic metabolism

EFGWB 93-0834, DP barcode D192580 -- submission of adsorption/desorption data -- DATA INCLUDED

Fathulla, R.N. The Adsorption and Desorption of ¹⁴C-Propanil on Typical Agricultural Soils. performed by Hazleton Laboratories America, Inc. Madison, WI. sponsored by Cedar Chemical Corporation, Memphis, TN. dated 5/24/90, received EPA 5/20/93 under MRID# 427804-01.

EFGWB 93-0855, DP barcode D192651 -- submission of soil photolysis data -- DATA INCLUDED

Reynolds, J.L. Soil Photolysis of ¹⁴C-Propanil. performed by XenoBiotic Laboratories, Inc., Plainsboro, NJ, and submitted by Rohm and Haas Company, Spring House, PA. received by EPA 6/24/93 under MRID 428204-01

5. REVIEWED BY:

Typed Name: E. Brinson Conerly-Perks
Title: Chemist, Review Section 3
Organization: EFGWB/EFED/OPP

E.B. Conerly-Perks 8/26/93

6. APPROVED BY:

Typed Name: Akiva Abramovitch
Title: Head, Review Section 3
Organization: EFGWB/EFED/OPP

Akiva Abramovitch
AUG 26 1993



7. CONCLUSIONS:

EFGWB 92-0122, DP barcode D170393 -- response to EFGWB review of aerobic soil metabolism study -- no data included

The data requirement is now satisfied. EFGWB can accept the referenced study together with the additional information provided in the current submission. A copy of the letter containing the agreement to test only one soil (Dr. Lynch to Dr. Abramson, 6/25/91, WTL 91-142) is attached.

EFGWB 92-0517, DP barcode D174696 -- aquatic field dissipation and irrigation water studies in Arkansas and Louisiana -- DATA INCLUDED

The studies are acceptable to fulfill the requirements for aquatic field dissipation at two locations. The data have a large amount of scatter, but this may be unavoidable in this type of field study, particularly since samples at or near the level of detection, as many were, are especially difficult to analyze precisely. There were distinct differences in the treatment of the control and test paddies in both cases; additional fertilizer was applied to the control, and different fungicides were used for the two paddies. The significance of these differences to the results of the studies is unknown.

In the Arkansas study:

Parent propanil was not detected in paddy or outflow water at any sampling interval, or in soil cores taken 164 days after the second treatment. Propanil concentration reached a peak (2.33 ± 0.45 ppm) in soil (sediment) on the day of the second treatment and remained high for the next 2 days; the concentration had fallen to close to quantitation limits by 14 days after the second treatment.

Solvent extractable metabolite 3,4-DCA reached a peak value for a single sample (2.70 ppm) in the 0-2 inch soil (sediment) layer on the day after the second treatment. The average concentrations in that layer were reasonably constant (0.64 to 1.46 ppm) for the next seven days. In paddy water, metabolite 3,4-DCA had a half-life of approximately 3 days.

In the Louisiana study:

Parent propanil was detected in paddy or outflow water only on the days of application. Propanil concentration in paddy water was highest on the day of the second application (2.3 ppm). Propanil concentration reached a peak (1.0 ppm) in soil (sediment) on the day of the first treatment; the concentration had fallen to close to quantitation limits by 7 days after the second treatment.

Solvent extractable metabolite 3,4-DCA reached peak value for a single sample (0.74 ppm) in the 0-2 inch soil (sediment) layer five days after treatment 2. The highest daily mean (0.45 ppm) occurred two days after application 2. Average concentrations in that layer were elevated above the level of detection for 120 days. In paddy water, metabolite 3,4-DCA had a half-life of approximately 2 days.

EFGWB 93-0023, DP barcode D183248 -- response to EFGWB review of aqueous photolysis, anaerobic and aerobic aquatic metabolism

The additional material provided in the current submission is acceptable to remove the deficiencies. These data requirements are fulfilled.

EFGWB 93-0834, DP barcode D192580 -- submission of adsorption/desorption data -- DATA INCLUDED

The study is not acceptable to fulfill data requirements. It is marginally acceptable to support rice use because conditions prevailing in rice paddies favor rapid degradation by metabolism and do not favor movement of parent.

To support terrestrial uses a new study is required. [EPA] standard procedure is to remove as much as possible of the supernatant before proceeding with the desorption step, although EFGWB does recognize that a small amount will unavoidably be left. In this case, the removal of supernatant from the adsorption phase was deliberately incomplete, leaving ca. 20% behind. This would tend to make larger amounts of material appear to desorb than was actually the case. The study report does not indicate that any kind of mathematical correction was used to adjust for the amount of material known to have been left in solution in the adsorption step. Since the desorption constants were estimated through this non-standard procedure, the desorption data cannot be interpreted with any confidence or used in ground water modelling efforts. These data are critical for final ground-water evaluation.

Results of the study suggest that propanil is only moderately mobile in sandy loam, silty clay loam, silt loam, or clay loam, but is highly mobile in sand. Plainfield sand had a k_d of adsorption of 0.538 and a k_{oc} of 306. California sandy loam had a k_d of adsorption of 2.32 and a k_{oc} of 239. Arizona silty clay loam had a k_d of adsorption of 5.79 and a k_{oc} of 703. Crowley silt loam had a k_d of adsorption of 8.00 and a k_{oc} of 800. Kewaunee clay loam had a k_d of adsorption of 11.7 and a k_{oc} of 389.

EFGWB 93-0855, DP barcode D192651 -- submission of soil photolysis data --DATA INCLUDED

The study is not acceptable to fulfill this data requirement which is called for to support terrestrial uses. However, EFGWB will not require a new study at this time, since it would add little useful information. The results are inadequate to define a half-life, but do suggest that "photolysis" on soil is actually largely due to metabolism by microbes, which is rapid. In fact, it appears to be more rapid in the dark. The investigator calculates an 11 day half-life for moist sandy loam exposed to light, but a 2-day half-life for dark controls. The slowing down of the degradative process in the light-exposed samples could be due to drying of the soil, as the investigator suggests. However, the longer degradation time for irradiated samples could also be due to the light exposure inhibiting the soil microbes, or other less obvious causes. The aqueous photolysis study also indicated lack of susceptibility to photodegradation. The study does not establish either a reliable half-life or a pattern of the appearance and decline of the degradates, and the deficiencies are such that upgrading does not seem possible. The major deficiency is that sampling was inadequate both in number and timing, and, therefore, calculation of a reliable value for the half-life is not possible. There were only two samples taken after day zero, and the concentrations of parent and degradate in those two samples were similar, making any calculations of a regression equation highly questionable. Also, the incubation was carried out only seven days. Although a 30-day study was mentioned in passing, those results were not reported. EFGWB believes that the 30-day study may not actually have been performed.

8. RECOMMENDATIONS:

EFGWB 92-0122, DP barcode D170393 -- response to EFGWB review of aerobic soil metabolism study

The registrant should be notified that the data requirement is fulfilled. EFGWB accepts the referenced study together with the additional information provided in the current submission. A copy of the letter containing the agreement to test only one soil (Dr. Lynch to Dr. Abramson, 6/25/91, WTL 91-142) is attached.

EFGWB 92-0517, DP barcode D174696 -- aquatic field dissipation and irrigation water studies -- DATA INCLUDED

The registrant should be notified that these studies are acceptable to fulfill the data requirement. No further data are required on aquatic field dissipation at this time.

bcp

Propanil 92-0122, -0517, 93-0023, -0834, -0855

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EFGWB 93-0023, DP barcode D183248 -- response to EFGWB review of aqueous photolysis, anaerobic and aerobic aquatic metabolism

The registrant should be notified that the previous studies together with the additional information are acceptable to fulfill the data requirements. No further data on aqueous photolysis, anaerobic or aerobic aquatic metabolism are required at this time.

EFGWB 93-0834, DP barcode D192580 -- submission of adsorption/desorption data -- DATA INCLUDED

The registrant should be informed that the study is marginally acceptable to support rice uses, but not acceptable to support terrestrial uses. A new study is required to support terrestrial uses. The new study should carefully address the desorption step, to insure complete removal of supernatant material following the adsorption step. These data are critical for final ground-water evaluation.

EFGWB 93-0855, DP barcode D192651 -- submission of soil photolysis data -- DATA INCLUDED

The applicant should be informed that the study is not acceptable. However, EFGWB believes no useful information would be gained by repeating the study, and, therefore, no additional data are required at this time.

9. BACKGROUND:

According to the 1987 Registration standard, 95% of the manufactured product is used on rice. The Propanil Task Force does not intend to submit data to support the terrestrial food uses (i.e. the 5% which is not rice).

ENVIRONMENTAL FATE ASSESSMENT

The data base for propanil for aquatic use (i.e. rice) is largely complete at this time. Propanil is subject to rapid metabolic degradation, and indications are strong that it will not persist in the field. Based on acceptable studies, it is rapidly metabolized under aerobic or anaerobic conditions in a water/sediment milieu ($t_{1/2}$ = 2-3 days). Acceptable aquatic field dissipation studies in rice paddies at two sites indicate short half-lives for propanil in the water (undetectable after no more than one day) and in the soil (sediment, ca. 2-7 days). The principal metabolic degradate, 3,4-DCA, reached a peak value in soil (sediment) 1 to 5 days after the second of two applications, remained high for 1 to 2 weeks, and was at or near detection limits for 4-6 months. Based on a acceptable study, propanil metabolizes rapidly in aerobic soil with a half-life of 0.5 days. However, propanil is stable to hydrolysis at pH 5, 7, and 9 in the laboratory, and, based on a marginally acceptable study, is stable to unsensitized aqueous photolysis. An unacceptable soil photolysis study also suggests stability to photodegradation; the observed transformation was due primarily to metabolic activity.

The available mobility studies indicate that under most conditions, propanil is not highly mobile. A partially acceptable batch adsorption/desorption study will support the aquatic uses, but is not acceptable to support the terrestrial uses. Adsorption parameters were as follows:

Plainfield sand k_d of adsorption = 0.538, k_{oc} = 306
California sandy loam k_d of adsorption = 2.32, k_{oc} = 239
Arizona silty clay loam k_d of adsorption = 5.79, k_{oc} = 703
Crowley silt loam k_d of adsorption = 8.00, k_{oc} = 800
Kewaunee clay loam k_d of adsorption = 11.7, k_{oc} = 389

The acceptable aquatic field studies also indicate that parent and metabolic degradate, 3,4-DCA, generally associate with soil rather than the aqueous phase. Detectable residues are confined largely to the top 2" of sediment.

Bioaccumulation data for fish have been waived based on the low k_{ow} of propanil.

GROUND WATER ASSESSMENT

In normal use (i.e. rice paddies), propanil does not possess the characteristics of potential to threaten ground water. The possible exceptions, sites of extreme vulnerability and low metabolic capacity would most probably occur only for terrestrial uses. Based on mobility criteria detailed above, propanil would be unlikely to reach ground water and due to its rapid metabolism in a water/soil matrix, would not be likely to persist.

SURFACE WATER ASSESSMENT

Due to both its lack of mobility and its rapid metabolic degradation in a water soil/matrix, propanil would not be likely to reach or to persist in surface water, in either the sediment or water phase.

DATA BASE ASSESSMENT

Data requirements for aquatic food use (i.e. rice) and their status:

hydrolysis -- stable at pH 5, 7, and 9. [pH 5 -- MRID# 410666-01 (EBC 1/10/92); pH 7, 9 -- ACC# 00111395 (REN 10/30/75)]

photolysis in water -- fulfilled [MRID# 410707-01 (EBC 1/10/92)]; stable to unsensitized aqueous photolysis

anaerobic aquatic metabolism -- fulfilled as of this review [MRID# 418726-01 (reviewed in EBC 1/10/92)]; additional information -- Propanil is rapidly metabolized under anaerobic conditions ($t_{1/2}$ = 2-3 days)

aerobic aquatic metabolism -- fulfilled as of this review [MRID# 418726-01 (reviewed in EBC 1/10/92)]; additional information -- Propanil is rapidly metabolized under aerobic conditions ($t_{1/2}$ = 2 days)

leaching/adsorption/desorption -- partially fulfilled, discussed in this review (MRID# 427804-01); additional data required for terrestrial crop use as noted above. Supernatant removal at the adsorption phase was deliberately incomplete, leaving ca. 20% behind, which would tend to make larger amounts of material appear to desorb than was actually the case. The study report does not indicate that any kind of mathematical adjustment was made for the amount of material known to have been left in solution in the adsorption step. Since the desorption constants were estimated through this non-standard procedure, the desorption data cannot be interpreted with any confidence. These data are critical for final ground-water evaluation.

Results of the study suggest that, except in sand, propanil is not highly mobile. Plainfield sand had a k_d of adsorption of 0.538 and a k_{oc} of 306. California sandy loam had a k_d of adsorption of 2.32 and a k_{oc} of 239. Arizona silty clay loam had a k_d of adsorption of 5.79 and a k_{oc} of 703. Crowley silt loam had a k_d of adsorption of 8.00 and a k_{oc} of 800. Kewaunee clay loam had a k_d of adsorption of 11.7 and a k_{oc} of 389. Plainfield sand had a k_d of adsorption of 0.538 and a k_{oc} of 306. California sandy loam had a k_d of adsorption of 2.32 and a k_{oc} of 239. Arizona silty clay loam had a k_d of adsorption of 5.79 and a k_{oc} of 703. Crowley silt loam had a k_d of adsorption of 8.00 and a k_{oc} of 800. Kewaunee clay loam had a k_d of adsorption of 11.7 and a k_{oc} of 389.

aquatic field dissipation -- fulfilled, discussed in this review (MRID# 422004-01, 422005-01) -- The studies are acceptable to fulfill the requirements for aquatic field dissipation at two locations. The data have a large amount of scatter, but this may be unavoidable in this type of field study.

In the Arkansas study, parent propanil was not detected in paddy or outflow water at any sampling interval, or in soil cores taken 164

days after the second treatment. Propanil concentration reached a peak (2.33 ± 0.45 ppm) in soil (sediment) on the day of the second treatment and remained high for the next 2 days; the concentration had fallen to close to quantitation limits by 14 days after the second treatment.

Solvent extractable metabolite 3,4-DCA reached a peak value for a single sample (2.70 ppm) in the 0-2 inch soil (sediment) layer on the day after the second treatment. The average concentrations in that layer were reasonably constant (0.64 to 1.46 ppm) for the next seven days.

In the Louisiana study, parent propanil was detected in paddy or outflow water only on the days of application. Propanil concentration in paddy water was highest on the day of the second application (2.3 ppm). Propanil concentration reached a peak (1.0 ppm) in soil (sediment) on the day of the first treatment; the concentration had fallen to close to quantitation limits by 7 days after the second treatment.

Solvent extractable metabolite 3,4-DCA reached peak value for a single sample (0.74 ppm) in the 0-2 inch soil (sediment) layer five days after treatment 2. The highest daily mean (0.45 ppm) occurred two days after application 2. Average concentrations in that layer were elevated above the level of detection for 120 days.

long term field dissipation -- EFGWB will not require additional data at this time; the conventional short term aquatic field dissipation study indicates that propanil will not persist; although the primary degradate, metabolite 3,4-DCA is detectable for 4 to 6 months

confined accumulation on rotational crops -- responsibility transferred to DEB

field accumulation on rotational crops -- responsibility transferred to DEB

confined accumulation on irrigated rotational crops -- responsibility transferred to DEB

fish bioaccumulation -- waiver recommended [EBC 4/26/89] due to low k_{ow} and applicant's affirmation of low accumulation in fathead minnows

The additional studies required for registration on terrestrial crops include:

photodegradation on soil -- not fulfilled -- MRID 428204-01 -- discussed in this review; no further data are being required at this time -
- The study is not acceptable, but provides some qualitative information which suggests that the primary degradative process which was occurring was metabolism. The study does not establish either a reliable half-life or a pattern of the appearance and decline of the degradates, and the deficiencies are such that upgrading it does not seem possible. The major deficiency is that sampling was inadequate both in number and timing, and, therefore, calculation of a reliable value for the half-life is not possible. There were only two samples taken after day zero, and the concentrations of parent and degradate in those two samples were similar, making any calculations of a regression equation highly questionable. Also, the incubation was carried out only seven days. Although a 30-day study was mentioned, the results were not reported, and apparently the study was not performed. The investigator calculates an 11 day half-life for moist sandy loam exposed to light, but a 2-day half-life for dark controls. The slowing down of the degradative process in the light-exposed samples could be due to drying of the soil, as the investigator suggests. However, the longer degradation time for irradiated samples could also be due to the light exposure inhibiting the soil microbes, or other less obvious causes.

aerobic soil metabolism -- fulfilled as of this review [MRID 415387-01 (reviewed in EBC 12/3/90)] -- a short half-life (0.5 days). The primary degradate was DCA, with a half-life of ca. 30 days.

anaerobic soil metabolism -- partially fulfilled by the anaerobic aquatic metabolism study [MRID# 418726-01 (EBC 1/10/92)]. The study provides the supplemental information that Propanil is rapidly metabolized under anaerobic conditions ($t_{1/2}$ = 2-3 days).

terrestrial field dissipation -- NOT FULFILLED -- will not be submitted by the Propanil Task Force

accumulation in confined rotational crops -- NOT FULFILLED -- will be submitted by the Propanil Task Force for rice

accumulation in field rotational crops -- conditionally required, if the confined study indicates uptake of residues of concern

EFGWB also required the following studies, listed below, which are not usually imposed for aquatic uses:

lab volatility
spray drift
downwind monitoring of deposition on other crops

10. DISCUSSION OF INDIVIDUAL TESTS OR STUDIES: see DERs
11. COMPLETION OF ONE-LINER: updated one-liner attached
12. CBI APPENDIX: attached to DERs



**ROHM
AND
HAAS
COMPANY**

July 25, 1991

Lois

Dr. Allan S. Abramson
Acting Director, Special Review
and Reregistration Division
U.S. Environmental Protection Agency
2nd Floor Mail Room
Crystal Mall #2
1921 Jefferson Davis Highway
Arlington, Virginia 22202

Dear Dr. Abramson:



Subject: .Propanil Registration Standard (Case #0226)
.Letter of June 17, 1991 to Dr. Roger Novak of NPC Incorporated
.Review of The Aerobic Soil Metabolism Study (MRID 41538701)

We received the above referenced letter and review document from Dr. Novak of NPC Incorporated. The letter and review document should not have been sent to Dr. Novak, the Technical Director of the Propanil Task Force, since the Task Force is only supporting aquatic propanil uses. The aerobic soil metabolism study was submitted to EPA by the Rohm and Haas Company in support of the terrestrial use of propanil. Other members of the Propanil Task Force are not supporting this use and, as far as we can tell, should not have registrations for terrestrial uses.

In your letter of June 17, 1991 two deficiencies in the aerobic soil metabolism study were cited and we were requested to respond to the Agency as to how we will address the deficiencies.

To address the first deficiency, additional information on intermediate degradates and reactions in the formation of the minor metabolite N-hydroxy-3,4-dichloroazobenzene were requested. We will provide this information within the requested 90-day time frame.

The second deficiency noted was that only one soil type was tested. The reviewer felt that, since propanil was used on wheat, a crop grown in various soil types with wide geographic distribution, testing was required on more than one soil type. However, STAMPEDE® (propanil) use on small grains is a minor use in a very limited region within four states for a very specific weed spectrum. STAMPEDE® is used only on spring wheat to control foxtail (and is not effective on wild oats). It is effective in this use because of a combination of the type of wheat treated, which is tolerant to propanil, and environmental conditions of the region which provide an application window in

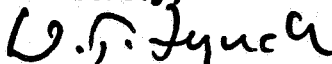
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8/3/91 10*

which both the crop and foxtail are in the proper growth stages. Propanil is not effective and will damage winter wheat crops grown outside the label specified four-state region. Under these circumstances, an aerobic soil metabolism study with more than one soil type should not be required for propanil. The soil sample used in the study was the standard type required in an aerobic soil metabolism study and it was obtained from, and is common to, the wheat-growing area where STAMPEDE® is used.

.....
In summary, we will provide the requested information relative to the formation of the minor metabolite in the propanil aerobic soil metabolism study, but request a waiver for a second aerobic soil metabolism study with a second soil type on the basis that propanil use on wheat is a minor use without widespread distribution.

If additional information is needed, please call me at 215-592-3190.

Sincerely,



William T. Lynch, Ph.D.
Product Registration Manager
Agricultural Chemicals Registration
and Regulatory Affairs Department

WTL/hew

DATA EVALUATION REVIEW 1

I. Study Type: photolysis on soil; guideline 161-3

II. Citation:

Reynolds, J.L. Soil Photolysis of ¹⁴C-Propanil. performed by Xenobiotic Laboratories, Inc., Plainsboro, NJ, and submitted by Rohm and Haas Company, Spring House, PA. received by EPA 6/24/93 under MRID 428204-01

III. Reviewer:

Typed Name: E. Brinson Conerly-Perks
Title: Chemist, Review Section 3
Organization: EFGWB/EFED/OPP

E. B. Conerly-Perks 8/26/93

IV. Conclusions:

The study is not acceptable and provides only qualitative information. However, because results suggest that "photolysis" on soil is actually largely due to metabolism by microbes, it appears that little information would be gained by requiring an additional study at this time. The aqueous photolysis study also indicated lack of susceptibility to photodegradation.

The study does not establish either a reliable half-life or a pattern of the appearance and decline of the degradates. The major deficiency is that sampling was inadequate both in number and timing, and, therefore, calculation of a reliable value for the half-life is not possible. There were only two samples taken after day zero, and the concentrations of parent and degradate in those two samples were similar, making any calculations of a regression equation highly questionable. Also, the incubation was carried out only seven days. Although a 30-day study was mentioned, it was not reported, and apparently not performed. The investigator calculates an 11 day half-life for moist sandy loam exposed to light, but a 2-day half-life for dark controls. The slowing down of the degradative process in the light-exposed samples could be due to drying of the soil, as the investigator suggests. However, the longer degradation time for irradiated samples could also be due to the light exposure inhibiting the soil microbes, or other less obvious causes.

V. Materials and Methods:

ABSTRACT

Soil for the soil photolysis of propanil was obtained from a representative-use area in North Dakota and was of the same classification as the soil used in the aerobic soil metabolism study.

In order to set the sampling interval for a 30-day photolysis study, two seven-day studies were conducted. [The 30-day study was not reported -- B C-P]. The photodegradation of propanil 3,4-dichloropropionanilide) was examined in a sandy loam soil. Propanil did not degrade in air-dried soil under simulated sunlight (xenon arc lamp) at ~23-24°C. However, when propanil was applied to moistened soil, a half-life of approximately 11 days was observed in the irradiated samples versus a half-life of approximately 2 days in the dark controls, indicating that degradation was due to soil metabolism not photolysis. Furthermore, any metabolite that was found in the irradiated samples was also found in the dark controls, thus supporting the argument that degradation was due to soil metabolism not photolysis.

Air-dried soil samples irradiated with intermittent light and dark cycles of 12 hours each day for 7 days. Samples were harvested on days 0, 3, and 7 post-treatment. An additional 7-day study was also conducted with the soil @ 75% field moisture capacity. Propanil uniformly labeled with carbon-14 in the ring position was used in the study at a treatment rate of ~5 parts per million (ppm [$\mu\text{g/g}$]). The radiolabeled test substance had a specific activity of 20.56 mCi/g. The experimental set up for the study was designed to trap any volatile materials. Analyses were conducted by solvent-solvent extraction, liquid scintillation counting (LSC), thin layer chromatography (TLC), and high performance liquid chromatography (HPLC) with radiometric detection. Samples were analyzed chromatographically by normal phase TLC and reversed phase HPLC.

Materials

test material -- ring U-¹⁴C-propanil, ~92% radiopure by TLC as supplied, repurified by TLC in toluene/acetonitrile (9/1) to 100% by TLC and 97.76% by HPLC.

test solution -- 5 ppm; -9.96 μg applied for experiment 1, -9.81 μg applied for experiment 2

test soil -- sandy loam (characteristics attached) sieved through 2-mm sieve before textural analysis. Soil layers were prepared to a thickness of -1.3 mm (2 gm soil with 2 ml H_2O)

light source -- xenon arc lamp, comparable in intensity and spectrum to measured values for natural sunlight in the local area where the experiment was performed

photolysis chamber -- temperature controlled, 12 hour on/ 12 hour off light cycle

Method

incubation -- a total of 16 soil-layered dishes were used in each experiment. In experiment 1 (with dry soil), the test material was dissolved in methylene chloride, and in the second experiment (with moist soil), in ethanol. Dark controls were wrapped in aluminum foil. Samples were taken at 0, 3, and 7 days of both light-exposed and dark control samples. The incubation chamber was connected to a series of traps which collected the entire volatile output of all dishes in the chamber.

extraction and fractionation of soil samples -- Each soil layer was extracted with acetonitrile/acidified water, filtered, and the filtrate extracted with methylene chloride. The filtrate and both layers from the MeCl_2 extraction were analyzed by LSC. The organic extract was concentrated by rotary evaporation.

analysis

LSC -- original filtrate, extracts, extracted soils after combustion

TLC -- on silica gel in toluene/acetonitrile -- concentrated organic extract

HPLC -- reversed phase, using a water/methanol solvent system -- representative day-7 extracts

VI. Study Author's Results and/or Conclusions:

RESULTS AS REPORTED BY THE STUDY AUTHOR:

In the first experiment the majority of radioactivity from the air-dried soil was extracted into the acetonitrile/water layer (>99%) and partitioned with methylene chloride. Radioactivity remaining in the aqueous fractions and volatiles was minimal (< 0.13% of the applied radioactivity). The maximum level of unextracted radioactivity from either the irradiated or the dark control samples was observed on day 3, 1.90% of the total recovered radioactivity. Overall recoveries of the applied radiochemical ranged from 99.67% to 105.09% for air-dried soil samples.

The major radioactive component was propanil in the organosoluble fraction ($\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$) from both the irradiated and dark control air-dried soil samples showed, accounting for >98% of the radioactivity.

Assuming pseudo-first-order kinetics, the half-life of propanil under air-dried soil test conditions was calculated to be approximately 333 days for the irradiated samples and approximately 90 days for the dark control samples.

The second experiment, conducted with soil moistened to 75% field moisture capacity, showed a different pattern of extraction than that of the first experiment and a significant difference between the dark controls. The

irradiated samples showed slower degradation than the dark control. On day 0, 95.15% of the total applied radioactivity was partitioned into the methylene chloride/acetonitrile ($\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$) fraction. Less than 0.80% was detected in either the aqueous and/or the PES fraction. By day 7, 74.21% of the total ^{14}C recovered from the irradiated samples was partitioned into the $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ fraction. The radioactivity remaining in the solids after extraction accounted for 20.65% of total applied radioactivity. Less than 0.70% of the radioactivity was found in the aqueous fraction, and 0.08% was detected in the trapped volatiles.

The day-7 dark control samples showed that 40.92% of the total applied radioactivity was partitioned into the $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ fraction. The level of radioactivity found in the aqueous fraction amounted to 1.27% of the total applied radioactivity. The PES fraction contained 47.62% of the total applied radioactivity. Trapped volatiles amounted to less than 1% of the applied radioactivity. Overall recoveries of applied radiochemical for the irradiated and dark control samples ranged from 89.88% to 95.93%.

TLC analysis of the $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ fraction from extraction of irradiated moistened soil samples showed the major radioactive component, which amounted to 58.62% of the applied radioactivity on day 7, to be the parent compound. However, three additional degradates designated as Met 1, Met 3, and Met 5 were also detected. On day 3, Met 1 amounted to 5.70% of the applied radioactivity. By day 7, Met 1 had decreased to 2.72%. Met 3, however, remained fairly constant between the day-3 and day-7 sampling intervals (2.67% and 2.81%, respectively). The degradate designated as Met 5 increased from 2.43% on day 0 to 10.07% of the applied radioactivity by day 7. Met 1 had a ratio-to-front (R_f) value similar to one of the reference standards, namely 3,4-dichloroaniline; however, further analysis of the extracts by reversed phase HPLC indicated that Met 1 was not 3,4-dichloroaniline. It should be noted that Metabolites 1, 3, and 5 were also found in the dark control samples.

In the organosoluble fraction from moistened dark control samples, additional degradates were detected. Met 2, Met 4, and several unresolved degradates specified as "Misc. Unk." (i.e., miscellaneous unknowns) were observed in the day-3 sample; however, by day 7, Met 2 and Met 4 were not detected. Parent compound accounted for a maximum of 6.40% of the total applied radioactivity in the day-3 sample. Two major degradates amounting to 10.49% and 21.21% of the total applied radioactivity were observed on day 3, namely Met 3 and Met 5. By day 7, these degradates had decreased to 2.95% and 13.89%, respectively. Met 1 increased from 5.82% on day 3 to 8.39% of the total applied radioactivity by day 7. By day 7, the degradates specified as "Misc. Unk." were resolved into one major unknown, which accounted for 10.23% of the total applied ^{14}C .

CONCLUSIONS AS REPORTED BY THE STUDY AUTHOR:

The conclusions drawn from these experiments are that photolysis in soil is not a significant degradative pathway for propanil and that the observed degradation is a result of soil metabolism not photolysis. This conclusion is further supported by the ultraviolet-visible spectrum of propanil, the aerobic soil metabolism study, and the aqueous photolysis study.

Assuming pseudo-first-order kinetics, the half-life of propanil under the given test conditions using soil moistened to 75% field moisture capacity was calculated to be approximately 11 days for the irradiated samples and approximately 2 days for the dark control samples.

One very significant observation is that any metabolite observed in the irradiated sample was also observed in the dark control sample. This indicates that the formation of metabolites is not caused by photolysis.

The short half-life (2 days) observed in the dark control samples in the moistened soil agrees with the 0.5-day half-life found in the aerobic soil metabolism study. Additionally, after 7 days, the observed 47.62% PES

fraction (bound residues) accords with the 62% bound residue observed after 7 days in the aerobic soil metabolism study.

The longer half-life (11 days) for the irradiated samples can be attributed to drying of the soil under the light source, thereby slowing down the aerobic soils metabolism rate in the soil.

The ultraviolet and visible spectrum of propanil shows no absorption from 300 to 700 nm, which suggests that photolysis is not a major degradative pathway.

An aqueous photolysis study gave half-lives of approximately 103 and 737 days for the irradiated and dark samples, respectively.

VII. Reviewer's Comments:

The study is not acceptable, and the deficiencies are such that upgrading it does not seem possible. The results suggest that "photolysis" on soil may be largely due to metabolism by soil microbes. This position is supported by the results of the aqueous photolysis study, which also indicated lack of susceptibility to photodegradation.

- 1) Sampling was inadequate to permit calculation of a reliable value for the half-life, both in number and timing. There were only two samples taken after day zero, and the concentrations of parent and degradate in those two samples were similar.
- 2) The incubation was not carried out even to one half-life. Therefore, this study does not establish either a reliable half-life or a pattern of the appearance and decline of the degradates. The investigator does mention a 30-day study which was not reported, and apparently not performed.

The slowing down of the degradative process could be due to drying of the soil, as the investigator suggests. However, the longer degradation time for irradiated samples could also be due to inhibitory effects of light exposure or other less obvious causes.

VIII. CBI Information Addendum:

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DATA EVALUATION REVIEW 2

I. Study Type: Mobility -- adsorption/desorption; guideline 163-1

II. Citation:

Fathulla, R.N. The Adsorption and Desorption of ¹⁴C-Propanil on Typical Agricultural Soils. performed by Hazleton Laboratories America, Inc. Madison, WI. sponsored by Cedar Chemical Corporation, Memphis, TN. dated 5/24/90, received EPA 5/20/93 under MRID# 427804-01.

III. Reviewer:

Typed Name: E. Brinson Conerly-Perks
Title: Chemist, Review Section 3
Organization: EFGWB/EFED/OPP

E.B. Conerly-Perks 8/26/93

IV. Conclusions:

The study is marginally acceptable to fulfill data requirements for aquatic (rice) use, since these conditions favor rapid degradation and do not favor mobility. However, it is not acceptable to fulfill data requirements for terrestrial use. A new study is required to support the terrestrial uses.

[EPA] standard procedure is to remove as much as possible of the supernatant before proceeding with the desorption step, although EFGWB does recognize that a small amount will unavoidably be left. In this case, the removal of supernatant from the adsorption phase was deliberately incomplete, leaving ca. 20% behind. This would tend to make larger amounts of material appear to desorb than was actually the case. The study report does not indicate that any kind of mathematical correction was made for the amount of material known to have been left in solution in the adsorption step. Since the desorption constants were estimated through this non-standard procedure, the desorption data cannot be interpreted with any confidence. These data are critical for final ground-water evaluation.

Results of the study suggest that, except in sand, propanil is not highly mobile. Plainfield sand had a k_d of adsorption of 0.538 and a k_{oc} of 306. California sandy loam had a k_d of adsorption of 2.32 and a k_{oc} of 239. Arizona silty clay loam had a k_d of adsorption of 5.79 and a k_{oc} of 703. Crowley silt loam had a k_d of adsorption of 8.00 and a k_{oc} of 800. Kewaunee clay loam had a k_d of adsorption of 11.7 and a k_{oc} of 389.

V. Materials and Methods:

ABSTRACT

The adsorption and desorption characteristics of 3,4-dichloropropionanilide-ring UL-¹⁴C (¹⁴C-Propanil) was studied on five representative agricultural soils using batch equilibrium. Soil-solution samples were prepared for each soil type in 0.509-, 1.02-, 5.10-, and 10.2- μ g/mL solutions of ¹⁴C-propanil in aqueous 0.01M calcium nitrate [Ca(NO₃)₂]. The samples were equilibrated for 24 hours at 25°C and then centrifuged. The supernatant was analyzed by liquid scintillation counting (LSC) to determine the disappearance of radioactivity from solution as a measure of test material adsorption to soil. Solution removed from each sample for analysis was replaced by an equal volume of unfortified aqueous 0.01M Ca(NO₃)₂. The samples were equilibrated for 24 hours at 25°C and the supernatant was analyzed by LSC to determine desorption.

Linear regression analysis of the adsorption data demonstrated that the plot of the soil and solution log concentrations of ¹⁴C-propanil at the concentrations tested was linear for all soil types (correlation coefficient of at least 0.913), indicating that the adsorption of ¹⁴C-propanil followed the Freundlich equation. The adsorption and desorption equilibrium constant (k_d) and sorption coefficient (k_{oc}) values determined in this study are summarized below:

soil type	adsorption		desorption	
	k_d	k_{oc}	k_d	k_{oc}
Plainfield sand	0.538	306	2.11	1200
CA sandy loam	2.32	239	3.03	312
AZ silty clay loam	5.79	703	7.11	863
Crowley silt loam	8.00	800	12.6	1260
Kewaunee clay loam	11.7	389	14.1	480

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Radiolabeled propanil was soluble and stable in aqueous 0.01M Ca(NO₃)₂ at the concentrations tested. Radiolabeled propanil adsorbed to all soils tested: in general, the amount of adsorption as measured by the calculated k_d values increased as the amount of organic matter in the soil increased. Radiolabeled propanil had a greater tendency to desorb from those soils with a lower adsorption k_d value. The material balance of selected soil-solution samples for each soil type ranged from 94.0% to 103.7% indicating that any radioactivity lost because of volatility or adsorption to the sample container was minimal.

Based on estimations of relative mobility using calculated soil thin layer chromatography R_f and k_{ow} values, the leaching potential of propanil from most agricultural soils would be low.

Materials

test material -- U-phenyl-ring labelled ¹⁴C-propanil; spec. act. 20.56 mCi/gm; radiopurity 98.5 (by performing lab by TLC)

test soil -- classifications and characteristics attached

Methods

After preliminary investigations, 2 each of the five different soil samples of approx. 2 gm were treated with 10 ml of 0.509, 1.02, 5.10, and 10.2 µg/mL solution of ¹⁴C-propanil. The preparations were shaken for approx. 24 hours @ 25°C, removed and centrifuged. For each sample an 8.00-mL aliquot of supernatant was removed, and duplicate 1.00 mL aliquots were analyzed by LSC. The LSC data were used to calculate the adsorption of ¹⁴C-propanil to soil. After completion of the adsorption phase, 8.00 mL of fresh, unfortified aqueous Ca(NO₃)₂ was added to each sample container to reestablish the 10.0 mL solution volume. The tubes were capped and placed in a shaking water bath at approximately 25°C. After approximately 24 hours, the samples were removed from the shaking water bath and centrifuged. Duplicate 1.00 mL aliquots of the supernatant were analyzed by LSC. The LSC data were used to calculate the desorption of ¹⁴C-propanil from soil.

VI. Study Author's Results and/or Conclusions:

VII. Reviewer's Comments:

The study is not acceptable to fulfill data requirements, since the desorption constants were not derived through [EPA] standard procedure of removing as much as possible of the supernatant before proceeding with the desorption step. The data cannot be interpreted with any confidence and derived values for adsorption and desorption cannot be considered accurate in this case. Results of the study suggest that, except in sand, propanil is not highly mobile.

The removal of supernatant from the adsorption phase was deliberately incomplete, leaving ca. 20% behind. This would tend to make larger amounts of material appear to desorb than was actually the case. It is understood that quantitative removal of the supernatant is a practical impossibility, but as much as possible should have been removed. The study report does not indicate that any kind of mathematical correction was made for the amount of material known to have been left in solution in the adsorption step.

VIII. CBI Information Addendum: attached

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DATA EVALUATION REVIEW 3

I. Study Type: aquatic field dissipation, guideline 164-2

II. Citation:

Young, D.P., Jr., Palmer, D.A., Johnson, G.D., Krueger, H., Hutchinson, C. Aquatic Field Dissipation and Irrigation Water Residues of Propanil following Application of Propanil 4 EC to an Arkansas Rice Paddy. performed by Wildlife International Ltd., Easton, MD, and EN-CAS Analytical Laboratories, Winston-Salem, NC. received at EPA 2/12/92 under MRID# 422004-01

III. Reviewer:

Typed Name: E. Brinson Conerly-Perks
Title: Chemist, Review Section 3
Organization: EFGWB/EFED/OPP

E.B. Conerly-Perks
8/26/93

IV. Conclusions:

The study is acceptable to fulfill the requirements for aquatic field dissipation at one location. The data have a large amount of scatter, but this may be unavoidable in this type of field study. In addition, EFGWB notes that samples at or near the level of detection, as many were, are especially difficult to analyze precisely. It must be noted that "not detected" does not mean "not there".

Parent propanil was not detected in paddy or outflow water at any sampling interval, or in soil cores taken 164 days after the second treatment. Propanil concentration reached a peak (2.33 ± 0.45 ppm) in soil (sediment) on the day of the second treatment and remained high for the next 2 days; the concentration had fallen to close to quantitation limits by 14 days after the second treatment.

Solvent extractable metabolite 3,4-DCA reached a peak value for a single sample (2.70 ppm) in the 0-2 inch soil (sediment) layer on the day after the second treatment. The average concentrations in that layer were reasonably constant (0.64 to 1.46 ppm) for the next seven days.

V. Materials and Methods:

ABSTRACT

The purpose of the study was to: 1) determine the extent of propanil residue dissipation in soil and water under actual use conditions; and 2) measure propanil residues in flood water which may be released and used for irrigation. Soil samples were analyzed for solvent extractable propanil, and solvent extractable metabolite 3,4-DCA. Water samples were analyzed for solvent extractable propanil, solvent extractable metabolite 3,4-DCA, and for total residues as base releasable metabolite 3,4-DCA. Two rice paddies (one treatment, one control) were selected for the study. The fields had not received propanil applications for at least two years. SIAMTM M-4 (also referred to as PROPANIL 4 EC) was applied twice to the treatment field at the rate of 4 lbs a.i./A on June 16 and June 22, 1990. This resulted in the label maximum allowed seasonal application of 8 lbs a.i./A.

For sampling purposes, the treated paddy was divided into three approximately equal sections based on size and dimension. Within each section, a transect of 20 stations was established across the width of the paddy. On each sampling day, one station in each section was randomly selected for collecting paddy water and soil samples. Each station was sampled no more than once during the study. An additional water sampling station was located at the low point in the paddy from which natural discharge or manual draining of the paddy would occur. On the control paddy, samples were collected randomly from throughout the paddy. Samples were collected beginning the day prior to the first application and continuing until 254 days after the second application. Water management practices for the propanil applications were modified due to the unusual meteorological conditions in Arkansas during the spring and early summer. The treatment field was not flooded between the first and second propanil applications and the treatments took place six days apart rather than the proposed fifteen days. Flooding of the treatment paddy began within 24 hours after the second application. Following the applications the water management practices were typical for the study area. The flood level was maintained until draining prior to harvest. Highest daily means (ppm) for each analyte were as follows:

SOLVENT EXTRACTABLE PROPANIL

MATRIX	APPLICATION DAY	SAMPLES ANALYZED	MEAN	S.D.	RANGE
PADDY WATER	T2+1	1	-	-	<0.01
OUTFLOW WATER	T2+7	1	-	-	<0.01
0-2" SOIL	T2+0	3	2.3	0.55	1.8-2.9
2-4" SOIL	T2+0	3	0.08	0.11	0.01-0.21
4-8" SOIL	T2+5	3	0.03	0.02	0.01-0.05

SOLVENT EXTRACTABLE metabolite 3,4-DCA

MATRIX	APPLICATION DAY	SAMPLES ANALYZED	MEAN	S.D.	RANGE
PADDY WATER	T2+2	1	-	-	1.5
OUTFLOW WATER	T2+7	1	-	-	0.09
0-2" SOIL	T2+3	3	1.5	0.93	0.69-2.5
2-4" SOIL	T2+5	3	0.07	0.06	<0.01-0.13
4-8" SOIL	T2+1	3	0.31	0.52	<0.01-0.91

BASE RELEASABLE metabolite 3,4-DCA

MATRIX	APPLICATION DAY	SAMPLES ANALYZED	MEAN	S.D.	RANGE
PADDY WATER	T2+2	1	-	-	0.98
OUTFLOW WATER	T2+7	1	-	-	0.17

The following half-lives were calculated for propanil and its degradates:

ANALYTE	MATRIX	HALF-LIFE (DAYS)
PROPANIL	Soil	1.47
Extractable metabolite 3,4-DCA	Paddy Water	3.12
Extractable metabolite 3,4-DCA	Soil	9.51
Extractable metabolite 3,4-DCA	Soil + Paddy Water	9.35
Base Releasable metabolite 3,4-DCA	Paddy Water	7.16

Materials and Methods

test material -- STAM M-4, a 4 lb/gal EC formulation of propanil

study site -- two plots in Lonoke County, AR. The treated paddy was 45 acres in size. The control paddy was 80 acres.

test planting

test -- (1990) Tebonnet rice at 2 lb/A, fertilized 1x with 2-2-15; benomyl applied 1x. The field had been previously planted with soybeans (1989) and rice (1988). Soils were loams, sandy clay loams, and silty clay loams.

control -- (1990) Tebonnet rice at 3 lb/A, fertilized 3x [fertilized not specified, but may be the same as for the test plot]. Fenoxypop applied 1x and acifluorfen 2x. The field was fallow in 1988 and planted to soybeans in 1989. Soils were silt loams and silty clay loams.

study design

The treated paddy was divided into 3 approximately equal sections.

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Propanil was applied 2x @ 4 lb/A (total of 8 lb/A) to the treatment field. Due to the unusual meteorological conditions during spring and early summer, the field was not flooded between the first and second treatments, and treatments were only six days apart. Flooding was initiated within 24 hours after the second application, and the flood was maintained until draining prior to harvest.

The control paddy was as described above, but not treated with propanil.

sampling -- the schedule is detailed in Table II attached

treatment paddy -- Within each of the three sections a transect of 20 stations was established across the width of the paddy. On each sampling day one station in each section was randomly selected for collection of paddy water and soil. Water and soil samples were taken from the same sites and no station was sampled more than once. Additional water sampling was done at the low point in the paddy, where natural discharge or manual draining would occur. Pre-application and post-harvest soil samples were taken to a depth of four feet, if possible, in one-foot increments.

control paddy -- sampled at random locations throughout the study, on the same days as the treatment paddy was sampled.

analyses

soil and water -- capillary gas chromatography (log 0.01 ppm) for solvent extractable propanil, free metabolite 3,4-DCA, and "base releasable" metabolite 3,4-DCA

VI. Study Author's Results and/or Conclusions:

RESULTS AS DESCRIBED BY THE STUDY AUTHOR [edited by the reviewer]

Because of unusual weather conditions (heavy rains followed by less than usual precipitation before planting), planting was delayed and the proposed schedule was not followed.

Solvent extractable propanil was below the detection level in paddy water and outflow water. Propanil residues in soil were mainly in the top two inches. The highest soil residue was 2.9 ppm, on the day of application 2, which was also the day of the highest daily mean value (2.3 ppm). Propanil residues in soil were at or below detectable levels up to 164 days after the second application.

The highest residue value for solvent extractable metabolite 3,4-DCA in paddy water was 1.5 ppm, which occurred two days after the second application. In outflow water, the highest value detected was 0.09 ppm, seven days after the second application. Residues of solvent extractable metabolite 3,4-DCA were below detectable limits 14 days after the second application.

Solvent extractable metabolite 3,4-DCA residues were also largely confined to the top 2 inches of soil. In this layer, the highest value for solvent extractable metabolite 3,4-DCA (2.7 ppm) occurred one day following the second application. The highest daily mean (1.5 ppm) also occurred three days after the second application. Residues were still being found at the detection limit 164 days after the second application.

Residues of solvent extractable metabolite 3,4-DCA in paddy water and soil were added together for the days 0 to 30 after the second application when residues were present in both matrices.

The highest base releasable metabolite 3,4-DCA concentration in paddy water was 0.98 ppm, which occurred on the second day after the second application. In outflow water, the highest value measured was 0.17 ppm, which occurred

seven days after the second application. Base releasable metabolite 3,4-DCA residues were still detectable 60 days after the second application in paddy water and 14 days after the second application in outflow water.

No solvent extractable propanil residues were detected in the four foot solvent cores taken 131 days after the second application. Solvent extractable metabolite 3,4-DCA residues were detected in the top 2 inches of the four foot core (0.02 ppm) but were undetected at depths greater than 2 inches.

Field-fortified samples of soil (treatment site) and water (control) were analyzed after 32 and again at 48 weeks of frozen storage. Recoveries of solvent extractable propanil from soil were 44% and 65% at 32 weeks, and 34% and 47% at 48 weeks; solvent extractable metabolite 3,4-DCA recoveries were 15% and 19% after 32 weeks and 11% after 48 weeks.

Field-fortified paddy water samples were analyzed after 17 and 39 weeks of storage. Solvent extractable propanil recoveries were 76% and 82%, solvent extractable metabolite 3,4-DCA recoveries were 56% and 57%, and total residues as base releasable metabolite 3,4-DCA were 54% and 55%.

Laboratory-fortified samples were also analyzed. After 56 weeks of storage recoveries of solvent extractable propanil in soil were 101% and 106%. Solvent extractable metabolite 3,4-DCA recovery was 41%. Solvent extractable propanil recoveries from water ranged from 51% to 81%, and solvent extractable metabolite 3,4-DCA recovery ranged from 76% to 117% after 16 weeks of frozen storage.

Observed differences in field spiking and laboratory spiking recoveries is due to the fact that field spikes were added to room temperature samples which then required a finite amount of time to cool to freezing. This allowed time for metabolic and other processes to occur which lessened the amounts eventually recovered. Reaction of metabolite 3,4-DCA with humic material is particularly important, since the analytical methods employed will not recover these "bound" residues except as total residues (base releasable). EPA has granted the consortium a waiver from performing the total residue analysis for all samples.

CONCLUSIONS AS STATED BY THE STUDY AUTHOR

The dissipation half-life of propanil in soil was calculated to be 1.48 days over the interval of 0 to 7 days after the second application when dissipation appeared to be following first-order kinetics. Propanil was not detected in water during this interval.

The half-life of solvent extractable metabolite 3,4-DCA in paddy water was calculated to be 3.12 days over the interval of 2 to 7 days after the second application when dissipation appeared to be following first-order kinetics. The half-life for soil was calculated at 9.51 days over the interval of 0 to 30 days after the second application when dissipation appeared to be following first-order kinetics.

The half-life for all solvent extractable metabolite 3,4-DCA (the total of amounts in soil and water) in the system was calculated to be 9.35 days.

The half-life of base releasable metabolite 3,4-DCA in paddy water was calculated at 7.16 days over the interval of 1 to 14 days after the second application when dissipation appeared to be following first order kinetics.

VII. Reviewer's Comments:

The study is acceptable to fulfill the requirements for aquatic field dissipation at one location. The data have a large amount of scatter, but this may be unavoidable in this type of field study. In addition, EFGWB notes that samples at or near the level of detection, as many were, are especially difficult to analyze precisely. Note that "not detected" does not mean "not

there".

Parent propanil was not detected in paddy or outflow water at any sampling interval, or in soil cores taken 164 days after the second treatment. Propanil concentration reached a peak (2.33 ± 0.45 ppm) in soil (sediment) on the day of the second treatment and remained high for the next 2 days; the concentration had fallen to close to quantitation limits by 14 days after the second treatment.

Solvent extractable metabolite 3,4-DCA reached a peak value for a single sample (2.70 ppm) in the 0-2 inch soil (sediment) layer the day after treatment 2. Average concentrations in that layer were reasonably constant (0.64 to 1.46 ppm) for the next seven days.

There were distinct differences in the treatment of the control and test paddies; additional fertilizer was applied to the control, and different fungicides were used for the two paddies. The significance of these differences to the results of the study is unknown.

VIII. CBI Information Addendum: attached

RIN 1876-95

PRO.PANIL EFGWB REVIEW

Page _____ is not included in this copy.

Pages 73 through 78 are not included.

The material not included contains the following type of information:

- Identity of product inert ingredients.
- Identity of product impurities.
- Description of the product manufacturing process.
- Description of quality control procedures.
- Identity of the source of product ingredients.
- Sales or other commercial/financial information.
- A draft product label.
- The product confidential statement of formula.
- Information about a pending registration action.
- FIFRA registration data.
- The document is a duplicate of page(s) _____.
- The document is not responsive to the request.

The information not included is generally considered confidential by product registrants. If you have any questions, please contact the individual who prepared the response to your request.

DATA EVALUATION REVIEW 4

I. Study Type: aquatic field dissipation, guideline 164-2

II. Citation:

Young, D.P., Jr., Palmer, D.A., Johnson, G.D., Krueger, H., Hutchinson, C. Aquatic Field Dissipation and Irrigation Water Residues of Propanil following Application of Propanil 4 EC to an Louisiana Rice Paddy. performed by Wildlife International Ltd., Easton, MD, and EN-CAS Analytical Laboratories, Winston-Salem, NC. received at EPA 2/12/92 under MRID# 422005-01

III. Reviewer:

Typed Name: E. Brinson Conerly-Perks
Title: Chemist, Review Section 3
Organization: EFGWB/EFED/OPP

E.B. Conerly-Perks
8/26/93

IV. Conclusions:

The study is acceptable to fulfill the requirements for aquatic field dissipation at one location. The data have a large amount of scatter, but this may be unavoidable in this type of field study. In addition, EFGWB notes that samples at or near the level of detection, as many were, are especially difficult to analyze precisely. It must be noted that "not detected" does not mean "not there".

Parent propanil was detected in paddy or outflow water only on the days of application. Propanil concentration in paddy water was highest on the day of the second application (2.3 ppm). Propanil concentration reached a peak (1.0 ppm) in soil (sediment) on the day of the first treatment; the concentration had fallen to close to quantitation limits by 7 days after the second treatment.

Solvent extractable metabolite 3,4-DCA reached peak value for a single sample (0.74 ppm) in the 0-2 inch soil (sediment) layer five days after treatment 2. The highest daily mean (0.45 ppm) occurred two days after application 2. Average concentrations in that layer were elevated above the level of detection for 120 days.

There were distinct differences in the treatment of the control and test paddies; additional fertilizer was applied to the control, and different fungicides were used for the two paddies. The significance of these differences to the results of the study is unknown.

V. Materials and Methods:

ABSTRACT

The purpose of the study was to: 1) determine the extent of propanil residue dissipation in soil and water under actual use conditions; and 2) measure propanil residues in flood water which may be released and used for irrigation. Soil samples were analyzed for solvent extractable propanil, and solvent extractable metabolite 3,4-DCA. Water samples were analyzed for solvent extractable propanil, solvent extractable metabolite 3,4-DCA, and for total residues as base releasable metabolite 3,4-DCA. Two rice paddies (one treatment, one control) were selected for the study. The fields had not received propanil applications for at least two years. Propanil 4 (also referred to as PROPANIL 4 EC) was applied twice to the treatment field at the rate of 4 lbs a.i./A on May 4 and May 18, 1990. This resulted in the label maximum allowed seasonal application of 8 lbs a.i./A.

For sampling purposes, the treated paddy was divided into three approximately equal sections based on size and dimension. Within each section, a transect of 20 stations approximately 50 feet apart was established across the width of the paddy. On each sampling day, one station in each section was randomly selected for collecting paddy water and soil samples. Each station was sampled no more than once during the study. An additional water sampling station was located at the low point in the paddy from which natural discharge or manual draining of the paddy would occur. On the control paddy, samples were collected randomly from throughout the paddy. Samples were collected beginning the day prior to the first application and continuing until 270 days after the second application. Water management practices were typical for the study area. Both fields were flooded after seedlings had established. Water was drained from the treated field prior to both propanil applications and reflooding began within 24 hours after the second application. The flood level was maintained until draining prior to harvest. Highest daily means (ppm) for each analyte were as follows:

SOLVENT EXTRACTABLE PROPANIL

MATRIX	APPLICATION DAY	SAMPLES ANALYZED	MEAN	S.D.	RANGE
PADDY WATER	T1+0	1	-	-	2.1
OUTFLOW WATER	T1+0	2	4.1	1.8	2.8-5.3
0-2" SOIL	T1+0	3	0.69	0.39	0.25-1.0
2-4" SOIL	T1+0	3	0.02	0.01	<0.01-0.02
4-8" SOIL	T1+0	3	0.02	0.02	<0.01-0.05

SOLVENT EXTRACTABLE metabolite 3,4-DCA

MATRIX	APPLICATION DAY	SAMPLES ANALYZED	MEAN	S.D.	RANGE
PADDY WATER	T2+1	3	0.38	0.28	0.21-0.70
OUTFLOW WATER	T2+1	2	0.43	0.36	0.17-0.68
0-2" SOIL	T2+2	3	0.45	0.14	0.34-0.60
2-4" SOIL	T2+3	3	0.02	0.01	0.01-0.03
4-8" SOIL	T2+3	3	0.03	0.52	<0.01-0.05

BASE RELEASABLE metabolite 3,4-DCA

MATRIX	APPLICATION DAY	SAMPLES ANALYZED	MEAN	S.D.	RANGE
PADDY WATER	T2+0	3	1.5	0.84	0.72-2.4
OUTFLOW WATER	T1+0	2	3.3	0.85	2.7-3.9

The following half-lives were calculated for propanil and its degradates:

ANALYTE	MATRIX	HALF-LIFE (DAYS)
PROPANIL	Soil	1.29
Extractable metabolite 3,4-DCA	Paddy Water	2.05
Extractable metabolite 3,4-DCA	Soil	11.60
Extractable metabolite 3,4-DCA	Soil + Paddy Water	6.47
Base Releasable metabolite 3,4-DCA	Paddy Water	3.67

Materials and Methods

test material -- Propanil 4, a 4 lb/gal EC formulation of propanil

study site -- two plots in Jefferson Davis Parish, LA. The treated paddy was 27 acres in size. The control paddy was 35 acres.

test planting

test -- (1990) Mercury rice water seeded at 115 lb/A, fertilized 1x with 20-15-15 and 1x with 33% nitrogen; 2,4-D applied 1x. The field had been planted with rice since 1988. Soils were loams and clay loams.

control -- (1990) Skybonnet rice dry seeded at 130 lb/A, fertilized 4x [fertilizer not specified]. Ordram and 2,4-D were applied 1x each as was Furadan. The field was planted to winter wheat and soybeans in 1988 and soybeans in 1989. Soils were silt loams, loams, silty clay loams and clay loams.

study design

The treated paddy was divided into 3 approximately equal sections.

40

Propanil was applied 2x @ 4 lb/A (total of 8 lb/A) to the treatment field. Water was drained from the field prior to each propanil application and reflooding was initiated within 24 hours. The flood was maintained until draining prior to harvest.

The control paddy was similar, but not treated with propanil.

sampling -- the schedule is detailed in Table II attached

treatment paddy -- Within each of the three sections a transect of 20 stations was established across the width of the paddy. On each sampling day one station in each section was randomly selected for collection of paddy water and soil. Soil samples were composed of five approximately 8 inch cores. Water and soil samples were taken from the same sites and no station was sampled more than once. Additional water sampling was done at the low point in the paddy, where natural discharge or manual draining would occur. Pre-application and post-harvest soil samples were taken to a depth of four feet, if possible, in one-foot increments.

control paddy -- sampled at random locations throughout the study, on the same days as the treatment paddy was sampled.

analyses

soil and water -- capillary gas chromatography (log 0.01 ppm) for solvent extractable propanil, free metabolite 3,4-DCA, and "base releasable" metabolite 3,4-DCA

VI. Study Author's Results and/or Conclusions:

RESULTS AS DESCRIBED BY THE STUDY AUTHOR [edited by the reviewer]

Solvent extractable propanil was detected in paddy water and outflow water only on the days of application. The highest value in paddy water was 2.3 ppm, which occurred the day of the second application. The mean value from all three stations for the second application was 1.6 ppm. The highest daily mean was 0.69 which occurred on the day of the first application. The highest daily mean (4.1 ppm) occurred on the same day.

Propanil residues in soil were mainly in the top two inches. The highest soil residue was 1.0 ppm, on the day of application 1, which was also the day of the highest daily mean value (0.69 ppm). Propanil residues in soil were below detectable levels by seven days after the second application.

The highest residue value for solvent extractable metabolite 3,4-DCA in paddy water was 0.70 ppm, which occurred one day after the second application. The highest daily mean value in paddy water was 0.38 ppm, also occurring one day after the second application. In outflow water, the highest value detected was 0.68 ppm, and the highest daily mean was 0.43 ppm, both of which occurred one day after the second application. Residues of solvent extractable metabolite 3,4-DCA were below detectable limits 14 days after the second application.

Solvent extractable metabolite 3,4-DCA residues were also largely confined to the top 2 inches of soil. In this layer, the highest value for solvent extractable metabolite 3,4-DCA (0.74 ppm) occurred five days following the second application. The highest daily mean (0.45 ppm) occurred two days after the second application. Residues were still being found at the detection limit 180 days after the second application.

For calculation of half-life, residues of solvent extractable metabolite 3,4-DCA in paddy water and soil were added together for the days 0 to 30 after the second application when residues were present in both matrices.

The highest base releasable metabolite 3,4-DCA concentration in paddy water

was 2.4 ppm, which occurred on the day of the second application. The highest daily mean (1.5 ppm) also occurred the day of the second application. In outflow water, the highest value measured was 3.9 ppm, and the highest daily mean was 3.3 ppm, both of which occurred on the day of the first application. Base releasable metabolite 3,4-DCA residues were still detectable 60 days after the second application in paddy water and 30 days after the second application in outflow water.

The four foot soil cores taken 96 days after the second application were not analyzed for solvent extractable propanil or solvent extractable metabolite 3,4-DCA because no significant residues were detected in other soil samples lower than 2 inches.

Field-fortified samples of soil (treatment site) and water (control) were analyzed after 18 to 35 weeks of frozen storage. Recoveries of solvent extractable propanil from soil were 40% and 47% at 35 weeks; solvent extractable metabolite 3,4-DCA recoveries were 12% and 13% after 28 weeks and 15% and 18% after 35 weeks.

Field-fortified paddy water samples were analyzed after 34 weeks of storage. Solvent extractable propanil recoveries were 76% and 86%, solvent extractable metabolite 3,4-DCA recoveries were 128% and 147%, and total residues as base releasable metabolite 3,4-DCA were 75% and 70%.

Laboratory-fortified samples were also analyzed. After 56 weeks of frozen storage, solvent extractable propanil recoveries were 109% and 119%. Solvent extractable metabolite 3,4-DCA recovery declined to approximately 48% by week 56. After 17 weeks of storage recoveries of solvent extractable propanil in paddy water were 85% and 111%. Solvent extractable metabolite 3,4-DCA recovery ranged from 48% to 103%.

Observed differences in field spiking and laboratory spiking recoveries is due to the fact that field spikes were added to room temperature samples which then required a finite amount of time to cool to freezing. This allowed time for metabolic and other processes to occur which lessened the amounts eventually recovered. Reaction of metabolite 3,4-DCA with humic material is particularly important, since the analytical methods employed will not recover these "bound" residues except as total residues (base releasable). EPA has granted the consortium a waiver from performing the total residue analysis for all samples.

CONCLUSIONS AS STATED BY THE STUDY AUTHOR

The dissipation half-life of propanil in soil was calculated to be 1.29 days over the interval of 0 to 3 days after the second application when dissipation appeared to be following first-order kinetics.

The half-life of solvent extractable metabolite 3,4-DCA in paddy water was calculated to be 2.05 days over the interval of 0 to 7 days after the second application when dissipation appeared to be following first-order kinetics. The half-life for soil was calculated at 11.60 days over the interval of 0 to 14 days after the second application when dissipation appeared to be following first-order kinetics.

The half-life for all solvent extractable metabolite 3,4-DCA (the total of amounts in soil and water) in the system was calculated to be 6.47 days.

The half-life of base releasable metabolite 3,4-DCA in paddy water was calculated at 3.67 days over the interval of 1 to 14 days after the second application when dissipation appeared to be following first order kinetics.

VII. Reviewer's Comments:

The study is acceptable to fulfill the requirements for aquatic field dissipation at one location. The data have a large amount of scatter, but this may be unavoidable in this type of field study. In addition, EFGWB notes

that samples at or near the level of detection, as many were, are especially difficult to analyze precisely. Note that "not detected" does not mean "not there".

Parent propanil was detected in paddy or outflow water only on the days of application. Propanil concentration in paddy water was highest on the day of the second application (2.3 ppm). Propanil concentration reached a peak (1.0 ppm) in soil (sediment) on the day of the first treatment; the concentration had fallen to close to quantitation limits by 7 days after the second treatment.

Solvent extractable metabolite 3,4-DCA reached peak value for a single sample (0.74 ppm) in the 0-2 inch soil (sediment) layer five days after treatment 2. The highest daily mean (0.45 ppm) occurred two days after application 2. Average concentrations in that layer were elevated above the level of detection for 120 days.

There were distinct differences in the treatment of the control and test paddies; additional fertilizer was applied to the control, and different fungicides were used for the two paddies. The significance of these differences to the results of the study is unknown.

VIII. CBI Information Addendum: attached

RIN 1876-95

PRO.PANIL EFGWB REVIEW

Page is not included in this copy.

Pages 84 through 115 are not included.

The material not included contains the following type of information:

- Identity of product inert ingredients.
- Identity of product impurities.
- Description of the product manufacturing process.
- Description of quality control procedures.
- Identity of the source of product ingredients.
- Sales or other commercial/financial information.
- A draft product label.
- The product confidential statement of formula.
- Information about a pending registration action.
- FIFRA registration data.
- The document is a duplicate of page(s) .
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The information not included is generally considered confidential by product registrants. If you have any questions, please contact the individual who prepared the response to your request.

Environmental Fate & Effects Division
 PESTICIDE ENVIRONMENTAL FATE ONE LINE SUMMARY
 PROPANIL

Last Update on August 16, 1993

[V] = Validated Study [S] = Supplemental Study [U] = USDA Data

LOGOUT	Reviewer: BCP	Section Head:	Date:
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Common Name: PROPANIL

Smiles Code: Cl-c(ccc1NC(=O)CC)c(Cl)c1

PC Code # : 28201 CAS #: 709-98-8

Caswell #:

Chem. Name : 3,4-DICHLOROPROPIONANILIDE or
 N-(3,4-DICHLOROPHENYL) PROPANAMIDE

Action Type: Herbicide

Trade Names: BAY 30130; CHEM RICE; DPA; ERBAN; FW-734

(Formul'tn): EC; ULV; LV

Physical State:

Use : FOR POSTEMERGENCE APPLICATION TO KILL BARNYARD GRASS AND
 Patterns : VARIOUS OTHER WEEDS IN RICE.
 (% Usage) :

Empirical Form: C₉H₉Cl₂NO
 Molecular Wgt.: 218.08 Vapor Pressure: 4.00E -5 Torr
 Melting Point : °C Boiling Point: °C
 Log Kow : 2.28 pKa: e °C
 Henry's : 1.15E -7 Atm. M3/Mol (Measured) 5.74E -8 (calc'd)

Solubility in ...					Comments
Water	2.00E	2	ppm	@20.0 °C	
Acetone	E		ppm	e °C	
Acetonitrile	E		ppm	e °C	
Benzene	E		ppm	e °C	
Chloroform	E		ppm	e °C	
Ethanol	E		ppm	e °C	
Methanol	E		ppm	e °C	
Toluene	E		ppm	e °C	
Xylene	E		ppm	e °C	
	E		ppm	e °C	

Hydrolysis (161-1)

[V] pH 5.0: STABLE FOR 30 DAYS MRID 410666-01
 [V] pH 7.0: STABLE
 [V] pH 9.0: STABLE
 [] pH :
 [] pH :
 [] pH :

114

Environmental Fate & Effects Division
PESTICIDE ENVIRONMENTAL FATE ONE LINE SUMMARY
PROPANIL

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Photolysis (161-2, -3, -4)

[V] Water: STABLE FOR 30 DAYS MRID 410707-01

[] :
[] :
[] :

[S] Soil : the chief degradative process is metabolism

[] Air :

Aerobic Soil Metabolism (162-1)

[V] 0.5 DAYS

[]
[]
[]
[]
[]
[]
[]

Anaerobic Soil Metabolism (162-2)

[V] HALF-LIFE 2-3 DAYS IN RICE PADDY WATER AND SEDIMENT (FULFILLED BY
[] THE ANAEROBIC AQUATIC STUDY REPORTED BELOW, MRID# 418726-01)

[]
[]
[]
[]
[]
[]

Anaerobic Aquatic Metabolism (162-3)

[V] HALF-LIFE 2-3 DAYS IN RICE PADDY WATER AND SEDIMENT
[] MRID 418726-01

[]
[]
[]
[]
[]
[]

Aerobic Aquatic Metabolism (162-4)

[V] HALF-LIFE 2 DAYS IN RICE PADDY WATER AND SEDIMENT
[] MRID 418487-01

[]
[]
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[]
[]
[]

Environmental Fate & Effects Division
PESTICIDE ENVIRONMENTAL FATE ONE LINE SUMMARY
PROPANIL

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Soil Partition Coefficient (Kd) (163-1)

[S] PLAINFIELD SAND KDADS=0.538, KOC=306
[S] CA. SANDY LOAM KDADS=2.32, KOC=239
[S] AZ. SILTY CLAY LOAM KDADS=5.79, KOC=703
[S] KEWAUNEE DLAY LOAM KDADS=8.00, KOC=800
[]
[]

Soil Rf Factors (163-1)

[]
[]
[]
[]
[]
[]

Laboratory Volatility (163-2)

[]
[]

Field Volatility (163-3)

[]
[]

Terrestrial Field Dissipation (164-1)

[]
[]
[]
[]
[]
[]
[]
[]
[]
[]
[]

Aquatic Dissipation (164-2)

[V] T1/2 IN SOIL 2-3 DAYS, IN WATER<1DAY
["] T1/2 3,4-DCA IN SOIL < 1 WEEK, IN WATER 2-3 DAYS
[]
[]
[]
[]

Forestry Dissipation (164-3)

[]
[]

Environmental Fate & Effects Division
PESTICIDE ENVIRONMENTAL FATE ONE LINE SUMMARY
PROPANIL

Last Update on August 16, 1993

[V] = Validated Study [S] = Supplemental Study [U] = USDA Data

Long-Term Soil Dissipation (164-5)

[]
[]

Accumulation in Rotational Crops, Confined (165-1)

[]
[]

Accumulation in Rotational Crops, Field (165-2)

[S] WITH THE EXCEPTION OF SOYBEANS, ALL CROPS PLANTED
[] 2 WKS AFTER APPL. HAD NONDETECTABLE RESIDUES.

Accumulation in Irrigated Crops (165-3)

[]
[]

Bioaccumulation in Fish (165-4)

[V] FATHEAD MINNOWS, BCF = 69 X AND 111 X WITH 95% DEPURATION
[] IN 10 DAYS

Bioaccumulation in Non-Target Organisms (165-5)

[]
[]

Ground Water Monitoring, Prospective (166-1)

[]
[]
[]
[]

Ground Water Monitoring, Small Scale Retrospective (166-2)

[]
[]
[]
[]

Ground Water Monitoring, Large Scale Retrospective (166-3)

[]
[]
[]
[]

Ground Water Monitoring, Miscellaneous Data (158.75)

[]
[]
[]

Environmental Fate & Effects Division
PESTICIDE ENVIRONMENTAL FATE ONE LINE SUMMARY
PROPANIL

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[V] = Validated Study [S] = Supplemental Study [U] = USDA Data

Field Runoff (167-1)

[]
[]
[]
[]

Surface Water Monitoring (167-2)

[]
[]
[]
[]

Spray Drift, Droplet Spectrum (201-1)

[]
[]
[]
[]

Spray Drift, Field Evaluation (202-1)

[]
[]
[]
[]

Degradation Products

4-(3,4-dichloroanilino)-3,3',4'-trichloroazobenzene (reputed to be
stable in soil and in sunlight)
3,4-dichloroaniline (DCA)
CO₂
3,3',4,4'-tetrachloroazobenzene (TCAB)

Environmental Fate & Effects Division
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PROPANIL

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Comments

Roots of rice plants absorb propanil and translocate and metabolize the propionic acid moiety.
Soil Koc = 188

References:

Writer : PJH, EBC 11/7/91