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EFGWB Out:

JAN 10 1992

To: Product Manager 71 (Waldrop/Stowe)
Reregistration Division

From: Akiva D. Abramovitch, Ph.D., Head
Environmental Fate Review Section #3
Environmental Fate & Ground Water Branch
Environmental Fate and Effects Division (H7507C)

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

Henry Jacoby

Attached, please find the EFGWB review of...

Reg./File #: n.a.

Chemical Name: Propanil

Type Product: herbicide

Product Name: n.a.

Company Name: Rohm and Haas

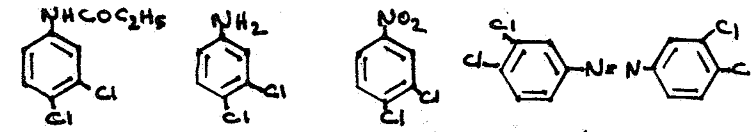
Purpose: submission of hydrolysis, aqueous photolysis, aerobic aquatic metabolism, anaerobic aquatic metabolism

Action Code: _____ EFGWB #(s): 91- 0619, 91-0665 Total Review Time: _____ days

| EFGWB Guideline/MRID Summary Table: The review in this package contains... | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 161-1 | 41066-01 | 162-1 | | 164-1 | | 165-1 | | 166-1 | |
| 161-2 | 410707-01 | 162-2 | | 164-2 | | 165-2 | | 166-2 | |
| 161-3 | | 162-3 | 418726-01 | 164-3 | | 165-3 | | 166-3 | |
| 161-4 | | 162-4 | 418487-01 | 164-4 | | 165-4 | | 167-1 | |
| 201-1 | | 163-1 | | 164-5 | | 165-5 | | 167-2 | |
| 202-1 | | 163-3 | | | | | | | |

1. **CHEMICAL**:

chemical name: 3,4-dichloropropionanilide, N-(3,4-dichlorophenyl) propanamide
common name: Propanil
trade name: n.a.
structure:



Propanil — 3,4-Dichloroaniline (DCA) — 3,4-Dichloronitrobenzene (DCNB) — 3,3',4,4'-tetrachloroazobenzene (TCAB)

CAS #: 709-98-8
Shaughnessy #: 28201

2. **TEST MATERIAL**: described in DERs

3. **STUDY/ACTION TYPE**:

91-0619 -- submission of hydrolysis (pH 5), aqueous photolysis, aerobic aquatic metabolism

91-0665 -- submission of anaerobic aquatic metabolism

4. **STUDY IDENTIFICATION**:

Spare, W.C. Hydrolysis of $^{14}$C-Propanil at pH 5. sponsored by the Propanil Task Force. performed by Agrisearch Incorporated, Frederick, MD. dated 1/16/89. rec'd EPA 4/18/89 under MRID# 410666-01.

Kesterson, A.L., Lawrence, B., Marsh, J.D., King, D.L., and Lawrence, L.J. Aqueous Photolysis of $^{14}$C Propanil in Natural Sunlight. sponsored by the Propanil Task Force. performed by Pharmacology & Toxicology Research Laboratory, Lexington, KY. dated 4/10/89. rec'd EPA 4/25/89 under MRID# 410707-01

Spare, W.C. Anaerobic Aquatic Metabolism of Propanil. sponsored by the Propanil Task Force. performed by Agrisearch Incorporated, Frederick, MD. dated 5/2/91. rec'd EPA 5/14/91 under MRID# 418726-01.

Spare, W.C. Aerobic Aquatic Metabolism of Propanil. sponsored by the Propanil Task Force. performed by Agrisearch Incorporated, Frederick, MD. dated 4/8/91. rec'd EPA 4/19/91 under MRID# 418487-01.

5. **REVIEWED BY**:

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

E. B. Conerly-Perks 11/7/91

6. **APPROVED BY**:

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

Akiva Abramovitch
JAN 7 1992

7. **CONCLUSIONS**:

**hydrolysis**

1) This study completes the fulfillment of the requirement for hydrolysis data. Propanil has previously been shown to be stable at pHs 7 and 9.

2) Propanil is stable at pH 5. No significant hydrolysis was observed over the 30 day experimental period.



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aqueous photolysis

1) The study, although seriously flawed, is marginally acceptable to fulfill the requirement for aqueous photolysis data.

2) It provides the information that unsensitized aqueous photolysis will not be an important degradative pathway for Propanil.

3) If photolysis occurred at a faster rate, this study would be unacceptable. However, in this case, even if the study were repeated, the estimated photolysis half-life of Propanil and its characterization as relatively stable to light would not be likely to change significantly.

4) The level of temperature control claimed by the applicant (± 0.3°) cannot be verified from the data in the submission. The apparent fluctuation in temperature is far greater than ± 0.3° -- the reported difference between minimum and maximum temperature during a single day was generally at least 5°, and on several days was more than 10°. This might be sufficient to affect the rate of the reaction. As a rule-of-thumb, the rate of a reaction would be expected to double if the temperature rises ten degrees. However, we note that only a summary of the available temperature data is given, and more complete details might justify the applicant's claim.

5) The extrapolated value for the half-life is well beyond the period of the experiment, and therefore not necessarily very accurate.

anaerobic aquatic metabolism

1) The study does not fulfill the requirement for anaerobic aquatic metabolism data at this time. It will become acceptable when certain inconsistencies in the description of extraction of bound material are resolved.

2) It provides the supplementary information that anaerobic metabolism in "active" water and sediment is rapid with a half-life of 2 to 3 days under experimental conditions.

aerobic aquatic metabolism

1) The study does not fulfill the requirement for aerobic aquatic metabolism data at this time. It will become acceptable when certain inconsistencies are satisfactorily explained:

   - the behavior of 3,4-dichloroaniline in sterile *vs* vital systems
   - the description of extraction of bound material

2) It provides the supplementary information that aerobic metabolism in "active" water and sediment is rapid with a half-life of 2 days under experimental conditions.

8. RECOMMENDATIONS:

1) hydrolysis -- The applicant should be informed that this data requirement is fully satisfied.

2) aqueous photolysis -- The applicant must provide a discussion explaining the basis for their statement regarding temperature control.

3) anaerobic aquatic metabolism -- The applicant must provide a revised description of the extraction of bound material (on page 17 of the current submission), since the actual procedure used cannot be discerned from the material submitted. In addition to a narrative description, a flow chart or diagram will also be appreciated.

4) **aerobic aquatic metabolism**

The applicant must provide at least a tentative explanation of the inconsistency in the behavior of 3,4-dichloroaniline in the sterile and vital systems. The applicant must also provide a revised description of the extraction of bound material (on page 16 of the current submission), since the actual procedure used cannot be discerned from the material submitted. In addition to a narrative description, a flow chart or diagram will also be appreciated.

9. BACKGROUND:

ENVIRONMENTAL FATE ASSESSMENT

The data base for Propanil is incomplete at this time, and therefore only very limited assessment can be made of its expected behaviour in the environment. 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. Based on partially acceptable studies, it is rapidly metabolized under aerobic or anaerobic conditions in a water/sediment milieu, and undergoes hydrolysis at a moderate rate in the same water/sediment system. These same studies indicate that degradates from metabolism prefer to associate with the soil phase rather than the aqueous phase, i.e. they become more immobile with time. Based on a partially acceptable study, Propanil metabolizes rapidly in aerobic soil with a half-life of 0.5 days. Other environmental fate data, which include leaching, anaerobic soil metabolism, aquatic metabolism, and field dissipation, are yet to be submitted.

GROUND WATER ASSESSMENT

Due to its rapid metabolism in a water/soil matrix, Propanil might not be likely to persist in ground water.

SURFACE WATER ASSESSMENT

Due to its rapid metabolism in a water soil/matrix, Propanil might not be likely to persist in surface water.

DATA BASE ASSESSMENT

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

hydrolysis -- stable at pH 5, 7, and 9. The pH 5 study is discussed in this review

photolysis in water -- fulfilled, discussed in this review. The study provides the marginally acceptable information that Propanil is stable for 30 days to unsensitized photolysis in water. Note that the extrapolated value for the half-life (103.3 days) is well beyond the experimental period, and therefore not necessarily accurate.

anaerobic aquatic metabolism -- partially fulfilled, discussed in this review. The study provides supplemental information that Propanil is rapidly metabolized under anaerobic conditions ($t_{½}$ = 2-3 days)

aerobic aquatic metabolism -- partially fulfilled, discussed in this review. The study provides supplemental information that Propanil is rapidly metabolized under aerobic conditions ($t_{½}$ = 2 days)

leaching/adsorption/desorption -- pending, also required for terrestrial crop use as noted above; to be submitted by the Propanil Task Force



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aquatic field dissipation -- pending, to be submitted by the Propanil Task Force

long term field dissipation -- conditionally required, if the conventional short term field dissipation study so indicates

confined accumulation on rotational crops -- pending, will be submitted by the Propanil Task Force

field accumulation on rotational crops -- requirement reserved pending results of confined study, also required for terrestrial uses

confined accumulation on irrigated rotational crops -- pending

fish bioaccumulation -- waiver recommended due to low $k_{ow}$ and applicant's affirmation of low accumulation in fathead minnows

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). The additional studies required for registration on terrestrial crops include:

photodegradation on soil -- **NOT FULFILLED** -- will not be submitted by the Propanil Task Force

aerobic soil metabolism -- partially fulfilled, supplemental information provided by MRID 415387-01 (EBC 12/3/90) which indicated 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 discussed in this review. The study provides the supplemental information that Propanil is rapidly metabolized under anaerobic conditions ($t_{½}$ = 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

Because of informal reports that Propanil applied to rice subsequently reached and damaged non-target crops, especially prune trees, EFGWB also requires the following studies, which are not usually imposed for aquatic uses:

lab volatility
spray drift -- EFGWB believes some studies have already been done. If this is the case, they should be submitted and evaluated before additional work is initiated
downwind monitoring of deposition on other crops -- for this special study, a protocol must be submitted and approved in advance. It should be designed to identify formulation type(s), if any, which inhibit or enhance migration of Propanil from the target crop.

10. DISCUSSION OF INDIVIDUAL TESTS OR STUDIES: See individual DER

11. COMPLETION OF ONE-LINER: attached

12. CBI APPENDIX: attached to DERs

DATA EVALUATION REVIEW 1

I. Study Type: hydrolysis, Guideline 161-1

II. Citation:

Spare, W.C. Hydrolysis of $^{14}$C-Propanil at pH 5. sponsored by the Propanil Task Force. performed by Agrisearch Incorporated, Frederick, MD. dated 1/16/89. rec'd EPA 4/18/89 under MRID# 410666-01.

III. Reviewer:

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

E.B. Conerly-Perks 11/7/91

IV. Conclusions:

1) This study completes the fulfillment of the requirement for hydrolysis data. Propanil has previously been shown to be stable at pHs 7 and 9.

2) Propanil is stable at pH 5. No significant hydrolysis was observed over the 30 day experimental period.

V. Materials and Methods:

Materials

test material -- [phenyl ring $^{14}$C]-Propanil, spec. act 20.56 µCi/mg, 99.2% radiopure

stock solution -- test material (described above) dissolved in acetonitrile to a final concentration of 10 ppm in pH 5 0.01 M acetate buffer

Methods

test conditions -- experimental solutions were maintained at 25 ± 1° C, and covered with aluminum foil to eliminate light. At the end of the experimental period a microbial plating check confirmed the sterility of all solutions.

sampling -- duplicate samples were taken at o, 1, 3, 7, 14, 21, and 30 days

analysis
TLC -- all samples were done in a single dimension in solvents 1 and 3; in addition, days 30 and 32 were run in two dimensions in solvents 2 and 3

solvent systems
toluene
acetone/toluene (15:85)
toluene/ethyl acetate (85:15)

LSC -- solutions, scraped spots

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

**ABSTRACT:**

This study was performed in response to the Propanil Registration Standard (12/23/87) which required measurement of the rate of hydrolysis of Propanil at pH 5. A single buffer system was prepared at pH 5 to test the solution hydrolysis of Propanil at a nominal rate of 10 ppm.

Analytical grade [phenyl ring-$^{14}$C-Propanil was prepared in acetonitrile. Aliquots of the solution were mixed with a portion of prepared buffer which had been previously sterilized by filtration. All buffer mixtures were incubated in the dark at 25 ± 1° C for up to 32 days. Samples of the buffers were removed at 0, 1, 3, 7, 14, 21, 30, and 32 days, spotted on thin-layer chromatography plates, and developed in two different and exclusive TLC solvents. A Berthold TLC Linear Analyzer was used to quantify the TLC plates.

The results demonstrated that Propanil was not hydrolyzed by exposure to buffered solutions at pH 5 for up to 32 days. Therefore, calculations to determine rate constant and half-life for Propanil at pH 5 were not performed.

Based on the results of this study, it can be concluded that Propanil is not affected by hydrolysis at pH 5. Therefore, hydrolysis may not be environmentally relevent.

<u>RESULTS AS DESCRIBED BY THE AUTHOR</u>

1) Both pH and concentrations of Propanil remained constant throughout the study. Greater than 95% of dosed radioactivity was Propanil after 30 days hydrolysis at pH 5 and 25 ± 1°C.

2) Material balance averaged greater than 92% for all samplings.

3) A sterility check conducted at the end of the study showed no bacterial growth from any test solution.

<u>CONCLUSIONS OF THE AUTHOR</u>

No significant hydrolysis of Propanil was observed over the test periods at pH 5. Therefore, hydrolysis of Propanil at pH 5 may not be environmentally relevant.

VII. Reviewer's Comments:

This study is acceptable to demonstrate the stability of Propanil at pH 5. It is unusual for a hydrolysis study to be done at only one pH. However, the stability of Propanil at pH 7 and 9 was demonstrated previously, and reported in the Registration Standard issued in 1987.

VIII. CBI Information Addendum: attached

RIN 1876-95

PROPANIL EFGWB REVIEW

Page ____ is not included in this copy.

Pages 8 through 13 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 2

I. Study Type: aqueous photolysis, guideline 161-2

II. Citation:

Kesterson, A.L., Lawrence, B., Marsh, J.D., King, D.L., and Lawrence, L.J. **Aqueous Photolysis of $^{14}$C Propanil in Natural Sunlight**. sponsored by the Propanil Task Force. performed by Pharmacology & Toxicology Research Laboratory, Lexington, KY. dated 4/10/89. rec'd EPA 4/25/89 under MRID# 410707-01

III. Reviewer:

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

IV. Conclusions:

The study is marginally acceptable to fulfill the requirement for aqueous photolysis data. However, we note that the reported data indicate at least the possibility that the temperature was too high and fluctuated over too wide a range. The study provides the information that unsensitized aqueous photolysis is a slow process ($t_{½}$ = 103 days) which will not be a major degradative pathway for Propanil. The extrapolated value for the half-life is well beyond the period of the experiment, and therefore not necessarily very accurate.

V. Materials and Methods:

materials

test compound -- specific activity 20.56 mCi/g (4.56x $10^{10}$ dpm), 99.7% radiochemically pure

test solution -- the test compound described above was dissolved in acetonitrile, then diluted with buffer to a final concentration of 19.5 ppm (8.9 x $10^2$ dpm)

methods

test conditions -- The quartz exposure tubes were connected in series to a series of two traps (ethylene glycol and 10% KOH). The tubes, immersed in a tank filled with deionized water, were exposed to direct sunlight throughout the study period.[1] The temperature was maintained at 24 ± 0.3°C.

controls -- identical to sample tubes but wrapped in aluminum foil to prevent exposure to light

sampling -- at 0, 5, 10, 15, 20, and 30 days

analysis

LSC -- total radioactivity

HPLC -- performed the same day as sampling, in a gradient methanol/water system

1 Exposure was at Lexington, Kentucky (latitude - 38.05 N; longitude 84.30 W), September 8 - October 8, 1988. Measured light energy during the 30 days of the study was 7.6 ± 2.4 W.min/cm2 per day.



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TLC -- used to confirm HPLC, spots quantitated by LSC

system A
first dimension -- toluene:ethyl acetate (85:15)
second dimension -- ethyl acetate:ethanol:ammonium hydroxide:water (40:40:4:20)

system B
first dimension -- toluene:ethyl acetate (85:15)
second dimension -- butanol:acetic acid:water (4:1:1)

NMR -- spectra of Propanil before and after irradiation with artificial light

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


ABSTRACT

Analytical grade ring-labelled $^{14}$C-Propanil was prepared in acetonitrile. An aliquot of this stock solution was aseptically added to an Erlenmeyer flask, the solvent allowed to evaporate, and a portion of sterile phosphate buffer (pH 7) was added to achieve a nominal concentration of 20 ppm. This final mixture was then placed in sample tubes which were exposed to natural sunlight continuously throughout the study period and maintained at 24 $\pm$ 0.3°C. One set of tubes was wrapped in aluminum foil to serve as dark controls. Samples were taken at 0, 5, 10, 15, 20, and 30 days for analysis by high performance liquid chromatography and thin layer chromatography.

The results demonstrated that $^{14}$C-Propanil degradation occured due to photochemical processes. The half-life of $^{14}$C-Propanil was determined to be 737.2 days for the dark control and 103.3 days in the irradiated samples.

The major degradation products were unknown polar degradates which totaled 10.0% at day 15 and 16.9% at day 30. NMR studies and thin layer chromatography showed these degradates to be a mixture of at least 10-15 different polar compounds, none of which accounted for > 4.2% of the total radiocarbon. 3,4-Dichloroaniline accounted for 0.7% in irradiated and 0.5% in dark control samples at day 15 and 0.7% in irradiated and 0.6% in dark control samples at day 30. An additional degradation product was $^{14}CO_2$ which amounted to 2.7% by day 30 in irradiated samples.


RESULTS AS DESCRIBED BY THE AUTHOR

After 30 days of irradiation, 76.9% of the total applied radiocarbon remained as parent compound. The dark controls were characterized as having 94% parent compound. HPLC analysis indicated a broad peak of polar degradates which were further characterized to be a mixture of at least 10-15 minor products. No individual photoproduct accounted for more than 4.2% of the total radioactivity. The large variety of polar products seem most likely to represent different isomeric substitutions of hydrolyl [*sic -- probably should be hydroxyl*] groups on the aromatic ring. Replacement of Cl with OH by nucleophilic displacement is a well established photochemical reaction. 3,4-Dichloroaniline (<1% in all samples) was detected in both dark control and irradiated samples.

CONCLUSIONS OF THE AUTHOR

Irradiated samples degraded more rapidly than dark control samples indicating that degradation was due to photochemical processes. The half-life for irradiated samples was 103.3 days while the half-life for dark control samples was 737.2 days.

VII. Reviewer's Comments:

1) The study is marginally acceptable to fulfill the requirement for aqueous photolysis data.

2) Unsensitized aqueous photolysis will not be an important degradative pathway for Propanil.

3) The level of temperature control claimed by the applicant ($\pm$ 0.3°) cannot be verified from the data in the submission. The apparent fluctuation in temperature is far greater than $\pm$ 0.3° -- the reported difference between minimum and maximum temperature during a single day was generally at least 5°, and on several days was more than 10°. This might be sufficient to affect the rate of the reaction. As a



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rule-of-thumb, the rate of a reaction would be expected to double if the temperature rises ten degrees. However, we note that only a summary of the available temperature data is given, and more complete details may justify the applicant's claim. The applicant should provide a discussion explaining the basis for their statement.

4) Note that the extrapolated value for the half-life is well beyond the period of the experiment, and therefore not necessarily very accurate.

VIII. CBI Information Addendum: attached



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RIN 1876-95

PROPANIL EFGWB REVIEW

Page_____ is not included in this copy.

Pages 17 through 32 are not included.

The material not included contains the following type of information:

- ____ Identity of product inert ingredients.
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- ____ Description of the product manufacturing process.
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- ____ Sales or other commercial/financial information.
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- ____ 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 3

I. Study Type: anaerobic aquatic metabolism, guideline 162-3

II. Citation:

Spare, W.C. Anaerobic Aquatic Metabolism of Propanil. sponsored by the Propanil Task Force. performed by Agrisearch Incorporated, Frederick, MD. dated 5/2/91. rec'd EPA 4/19/91 under MRID# 418726-01.

III. Reviewer:

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

E.B. Conerly-Perks 11/7/91

IV. Conclusions:

1) The study is not acceptable at this time to fulfill the requirement for anaerobic aquatic metabolism data. It will become acceptable when certain inconsistencies (discussed below) are resolved.

The study provides the supplemental information that anaerobic metabolism in "active" water and sediment is rapid with a half-life of 2 to 3 days under experimental conditions.

2) The applicant must provide a revised description of the extraction of bound material (on page 17 of the current submission), since the actual procedure used cannot be discerned from the material submitted. In addition to a narrative description, a flow chart or diagram will also be appreciated.

V. Materials and Methods:

materials

test compound -- uniformly ring labelled $^{14}C$-Propanil, sp. act. 19.39 $\mu Ci/mg$, average purity 99%. A solution of 22.7 mg in 2.3 ml acetonitrile was prepared and dosed at 50 $\mu l$/flask, resulting in a dose rate of 10.5 ppm relative to the water phase.

test matrixes -- sediment and water from the LSU Rice Research Station, Crowley, LA, details attached

methods

test conditions -- Incubation chambers were foil covered 125 ml Erlenmeyer flasks. For assessment of $^{14}CO_2$ evolution, two flasks ("12 month" samples) were connected to a series of 4 traps (ethylene glycol, $H_2SO_4$, and two KOH), and aerated by bubbling with nitrogen under positive pressure. In a second incubation, nitrogen was pulled through the 12 month vessels under negative pressure. All test systems were maintained at a temperature of 25 $\pm$ 1°C.

test method

**anaerobic incubation** -- Samples of 25 gm dry weight equivalent of silt loam sediment were flooded with rice paddy water and purged with nitrogen for 30 minutes. Bulk samples of 250 gm dry weight equivalent of sediment were prepared and incubated in parallel. All flasks were wrapped in foil and stoppered. They were then incubated for 1 month at 25 $\pm$ 1°C. $^{14}C$-Propanil was added, the flasks were incubated at 25 $\pm$ 1°C for two weeks, and a glucose amendment (1% of sediment dry weight) was added to promote conversion to anaerobic conditions. Flasks



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designated for 12 month sampling were connected to the apparatus depicted in figure 2 (attached). All flasks were flushed with nitrogen for 1 hour one day every other week.

**sterile incubation** -- Autoclave-sterilized samples of sediment and paddy water were prepared and incubated as above

sampling -- active preparations were sampled at 0, 1, 2, 3, 7, and 14 days, 1, 3, 6, 9, and 12 months. Sterile samples were analyzed at 2 and 12 months. Bulk samples were harvested at 4 months. Trapping solutions were analyzed for $^{14}CO_2$ and volatile metabolite production at each sampling period.

analyses
- total radioactivity -- LSC
- metabolites
  - extraction
    - water -- dichloromethane 3x
    - soil -- methanol/water (9:1) 3x
    - bound residues in methanol-extracted soil
      - *[reviewer's note] -- these procedures are described in a self-contradictory fashion which is, by design, not reproduced here and must be clarified.]*
  - TLC -- samples were developed in both systems below, with overspotted standards
    - toluene 100%
    - toluene/ethyl acetate 85:15
  - HPLC -- selected samples were analyzed in a methanol /water solvent system and monitored by a radioactive monitor
- humic/fulvic acids -- aliquots from selected NaOH extracts were acidified to pH 1-2 with concentrated HCl and allowed to precipitate for 48 hours under refrigeration (4 to 8°C). After centrifugation, supernatant (fulvic acid bound radioarbon was analyzed by LSC, and precipitate (humic acid bound radioactivity) was quantified by difference
- volatiles -- at each sampling interval, the amount of trapped radioactive volatiles and $^{14}CO_2$ was determined

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


ABSTRACT

Nearly all pesticides come into contact with soil, either through use or disposal. Upon incorporation into soil, pesticides can be metabolically transformed. The purpose of anaerobic aquatic metabolism studies is to determine the nature and extent of formation of pesticide degradation products under flooded conditions. These data may then be compared with the soil metabolism studies for possible novel modes of metabolism. Sterile conditions are also utilized to determine the nonbiological degradation of the pesticide.

Information from the anaerobic aquatic metabolism study is used to assess the formation of degradation products of a pesticide to which nontarget organisms may be exposed, and to facilitate assessment of potential disposal problems.

Water and sediment collected from the Louisiana State University Rice Research Station at Crowley, Louisiana, were received at Agrisearch. The sediment flooded with water was incubated anaerobically for 1 month prior to dosing. Following this incubation period, each test vessel was dosed with analytical grade [phenyl-ring-UL-$^{14}$C] Propanil at 10.5 ppm based on the water. Sterile sediment was preincubated for 1 month separate from the sterile water. Following preincubation, sterile water was dosed and added to the sediment. All incubations were performed at 25 ± 1° C. During the course of the study, samples from anaerobic (1, 2, 3, 7 and 14 days and 1, 2, 6, 9, and 12 months) and sterile (2 and 12 months) incubations were removed for extraction and identification of radioactive metabolites. Volatiles were trapped using a series of ethylene glycol, 1N $H_2SO_4$, and 1N KOH traps by flushing the headspace of duplicate representative incubation vessels with nitrogen.

Through 12 months anaerobic incubation of Propanil in microbiologically active sediment and water, production of volatile products was observed to be 3 to 4% of dose. The dose radioactivity was seen to migrate from the water to the sediment. Decline in the percent dose in the water occurred with a corresponding increase in the percent dose in the sediment. The calculated half-life and rate constant were 2 to 3 days and 2.3 to 3.9 days$^{-1}$, respectively.

The anaerobic metabolism pattern for Propanil was a rapid loss of parent with simultaneous production of 3,4-dichloroaniline. Dichloroaniline degradation occurred post 14 days with minor production of volatile products and strongly bound sediment products. These bound sediment products were released by base hydrolysis. Analysis showed the base releasable products to be very polar and associated with the fulvic and humic acids of the sediment.

RESULTS AS DESCRIBED BY THE AUTHOR

Under anaerobic conditions, the half-life of Propanil was 2 to 3 days (calculated by linear regression). The sterile preparations indicated a long half-life (130 to 594 days), but the data points showed poor correlation.

Metabolism in an anaerobic system of rice paddy [water] and sediment rapidly converted propanil to 3,4-dichloroaniline (DCA). Some of the DCA then became bound to sediment and increasingly resistant to solvent extraction with time. 3,4-Dichloroaniline peaked at day 14, when it represented 78% of applied radioactivity (water 13%, sediment 65%).

No radioactive peaks corresponding to 3,4-dichloronitrobenzene (DCNB) or 3,3',4,4'-tetrachloroazobenzene (TCAB) were observed. (Note that results are reported, which are the summation of radioactivity in the regions where these compounds would occur).

In the 366 day sterile sample, approximately 24% of the applied dose was Propanil, 27% DCA, 34% solvent soluble "polar" fulvic and humic acid associated compounds, and 20% base extractable.

Purity checks on the $^{14}$C-Propanil indicated an average purity of >99%.

Microbiological plating of sediment and water at 6 and 12 months showed viable populations in both media.

Radiocarbon balance was good for all samples (88.1 to 109.9% of dose under anaerobic conditions; 97.6 to 105.1% of dose under sterile conditions) except for the anaerobic day 273 sample which is considered spurious.

Bound radioactivity ranged from 12% at day 14 to >70% by 91 days, and remained relatively constant after that (70 to 85% of dose). Bound residues were extractable by means of exhaustive procedures including hydrolysis with a strong base. Base-extractable radioactivity in the sediment was very polar and was associated with fulvic, and to a lesser extent, humic acids in the sediment.

CONCLUSIONS OF THE AUTHOR

Propanil rapidly metabolized in anaerobic rice paddy water and sediment (half-life 2 to 3 days). The metabolism pattern was a rapid loss of parent with simulataneous production of 3,4-dichloroaniline in both sediment and water. Radiocarbon became increasingly bound to sediment with time. Decline in dichloroaniline concentration was observed post day 14 samplings. By day 91, 30% of radioactivity was very polar material solubilized by NaOH. It was not solvent extractable and was associated with fulvic and humic acids. These polar fulvic and humic acid associated products were the result of DCA degradation.

VII. Reviewer's Comments:

1) The study is not acceptable at this time to fulfill the requirement for anaerobic aquatic metabolism data. It will become acceptable when certain inconsistencies (discussed below) are resolved.

   It provides the supplementary information that anaerobic metabolism in "active" water and sediment is rapid with a half-life of 2 to 3 days under experimental conditions.

2) The applicant must provide a revised description of the extraction of bound material (on page 17 of the current submission), since the actual procedure used cannot be discerned from the material submitted. In addition to a narrative description, a flow chart or diagram will also be appreciated.

VIII. CBI Information Addendum: attached

RIN 1876-95

PRO.PANIL EFGWB REVIEW

Page _____ is not included in this copy.

Pages 36 through 53 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: aerobic aquatic metabolism, guideline 162-4

II. Citation:

Spare, W.C. Aerobic Aquatic Metabolism of Propanil. sponsored by the Propanil Task Force. performed by Agrisearch Incorporated, Frederick, MD. dated 4/8/91. rec'd EPA 4/19/91 under MRID# 418487-01.

III. Reviewer:

| | | |
|---|---|---|
| Typed Name: | E. Brinson Conerly-Perks | E. B. Conerly-Perks 11/7/91 |
| Title: | Chemist, Review Section 3 | |
| Organization: | EFGWB/EFED/OPP | |

IV. Conclusions:

1) The study is not acceptable at this time to fulfill the requirement for aerobic aquatic metabolism data. It will become acceptable when certain inconsistencies (discussed below) are resolved. It provides the supplementary information that aerobic metabolism in "active" water and sediment is rapid with a half-life of 2 days under experimental conditions.

2) 3,4 Dichloroaniline (DCA) is produced in the "sterile" system. This is at variance with the observations made in the hydrolysis and aqueous photolysis studies, where no such production occurred. These results could be explained if the "sterile" system regained some microbial activity during the course of the incubation. This seems to be ruled out by the plates which indicated no activity.

3) The behavior of DCA in the sterile and vital systems also seems to be inconsistent, since DCA apparently remains in the water in the sterile system while becoming bound to the soil in the vital system.

4) The applicant must provide a revised description of the extraction of bound material (on page 16 of the current submission), since the actual procedure used cannot be discerned from the material submitted. In addition to a narrative description, a flow chart or diagram will also be appreciated.

V. Materials and Methods:

materials

test compound -- uniformly ring labelled $^{14}C$-Propanil, sp. act. 20.52 $\mu$Ci/mg, average purity 99%.

test matrixes -- sediment and water from the LSU Rice Research Station, Crowley, LA, details attached.

methods

test method

**aerobic incubation** -- A solution of 10.0 mg/ml of acetonitrile was prepared and a large batch (1.5 l) of paddy water was dosed at a rate of 11.7 ppm. 25 gm of dry weight equivalent of sediment was placed into each of 12 Erlenmeyer flasks. The flasks were then flooded with 50 ml of dosed paddy water. All flasks were wrapped in foil. 8 were stoppered with polyurethane plugs and two were connected to the metabolism apparatus. They were then incubated at 25 $\pm$ 1°C. The flasks for volatile collection were flushed continuously at 40 to 60 ml/min during the work day using prehumidified compressed breathing air.

**sterile incubation** -- Autoclave-sterilized samples of sediment and paddy water were prepared and incubated as above

sampling -- active preparations were sampled at 0, 1, 3, 7, 14 and 30 days. Sterile samples were analyzed at 30 days. Trapping solutions were analyzed for $^{14}CO_2$ and volatile metabolite production at each sampling period.

analyses
- total radioactivity -- LSC
- non volatile metabolites
  - extraction
    - water -- dichloromethane 3x
    - soil
      - methanol/water (9:1) 3x
    - bound residues in methanol-extracted soil
      - [*reviewer's note] -- these procedures are described in a self-contradictory fashion which is, by design, not reproduced here and must be clarified.*]
  - TLC -- samples were developed in both systems below, with overspotted standards
    - toluene 100%
    - toluene/ethyl acetate 85:15
  - HPLC -- selected samples were analyzed in a methanol /water solvent system and monitored by a radioactive monitor
- humic/fulvic acids -- aliquots from selected NaOH extracts were acidified to pH 1-2 with concentrated HCl and allowed to precipitate for 48 hours under refrigeration (4 to 8°C). After centrifugation, supernatant (fulvic acid bound radioarbon was analyzed by LSC, and precipitate (humic acid bound radioactivity) was quantified by difference
- volatiles -- at each sampling interval, the amount of trapped radioactive volatiles and $^{14}CO_2$ was determined

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


<u>ABSTRACT</u>

Nearly all pesticides come into contact with soil, either through use or disposal. Upon incorporation into soil, pesticides can be metabolically transformed. The purpose of aerobic aquatic metabolism studies is to determine the nature and extent of formation of pesticide degradation products under flooded conditions. These data may then be compared with the soil metabolism studies for possible novel modes of metabolism. Sterile conditions are also utilized to determine the nonbiological degradation of the pesticide.

Information from the aerobic aquatic metabolism study is used to assess the formation of degradation products of a pesticide to which nontarget organisms may be exposed, and to facilitate assessment of potential disposal problems.

Analytical grade [phenyl-ring-UL$^{14}$C] Propanil was prepared in solution, mixed with rice paddy water at 11.7 ppm, and allowed to age in the dark under aerobic and sterile conditions over a rice paddy silt loam sediment. Sterile sediment was preincubated for 1 month separate from the sterile water. The incubations were performed at 25 $\pm$ 1° C. Rice paddy sediment and water were obtained from the LSU Rice Research Station, Crowley, LA, and used within 24 hours of field sampling. During the course of the study, samples from aerobic (0, 1, 3, 7, 14 and 30 days) and sterile (0 and 30 days) incubations were removed for extraction and identification of radioactive metabolites. Volatiles were trapped using a series of ethylene glycol, 1N $H_2SO_4$, and 1N KOH traps by flushing of the headspace with breathing air through duplicate representative incubation chambers.

Through 1 month aerobic incubation of Propanil in microbiologically active sediment and water, production of volatile products (4 to 8% of dose detected) was observed. The calculated half-life and rate constant of Propanil metabolism under these conditions were 2 days and $2.9^{-1}$ days$^{-1}$, respectively.

The aerobic aquatic metabolism pattern for propanil was a rapid loss of parent with simultaneous production of 3,4-dichloroaniline. Dichloroaniline degradation occurred post 7 days with production of volatile products and strongly bound sediment products. These bound sediment products were released by base hydrolysis. Analysis showed the base releasable products to be very polar and associated with the fulvic acids from the sediment.

Under sterile conditions, Propanil degraded to 3,4-dichloroaniline (DCA). No radiocarbon was associated with the sediment, all radioactivity was recovered in the water. After 30 days of abiotic (sterile) incubation, propanil represented about 21% of dose, DCA was approximately 72% and no unknowns were formed.




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RESULTS AS DESCRIBED BY THE AUTHOR

Under aerobic conditions, the half-life of Propanil was 2 days (calculated by linear regression). The metabolic degradation pathway of propanil in rice water and sediment was determined to be a rapid conversion of Propanil to 3,4-dichloroaniline (DCA). A portion of the DCA then became bound to the sediment and increasingly resistant to solvent extraction with time. Strong base hydrolysis released the majority of the nonextractable radioactivity of which DCA accounted for approximately 10% of dose at 30 days. The remaining NaOH releasable radioactivity was associated with fulvic acids and could not be resolved chromatographically. 3,4-Dichloroaniline production reached a maximum at day 7 when it accounted for 76% of the applied radioactivity; water 36%, sediment 39% No detectable 3,4-dichlorodinitrobenzene (DCNB) or 3,3',4,4'-tetrachloroazobenzene (TCAB) were observed in this study. Values assigned for these materials were for Rf region only, as no radioactive peaks were ever observed. Total summation of all regions so assigned was less than 1% of dose.

Sterile incubation of Propanil resulted in degradation of Propanil to 3,4-dichloroaniline. All radiocarbon remained in the water through the 30 day incubation. No unknowns were observed and Propanil was about 21% of dose with DCA at 72% of dose at 30 days. This indicates that abiotic hydrolysis of Propanil occurs in a soil-water system.

Purity checks on the $^{14}$C-Propanil indicated an average purity of 98.3%.

Microbiological plating of sediment and water at 0 and 30 days showed viable populations in both media. No growth was obtained from the sterile flasks.

Radioactivity balance during the study averaged 95.0% and 98.9% for aerobic and sterile samples, respectively.

CONCLUSIONS OF THE AUTHOR

Propanil was observed to rapidly metabolize in rice paddy water and sediment (half-life 2 days). The metabolism pattern was a rapid loss of parent with simulataneous production of 3,4-dichloroaniline in both sediment and water. Radiocarbon became increasingly bound to the sediment with time. $^{14}$C-DCA could be released from the sediment by strong base hydrolysis. By day 30, one-third of the bound residue was releasable DCA and two-thirds was very polar material solubilized by NaOH. This radioactivity was not solvent extractable and was associated with the fulvic acid fraction of the humic materials. Decline in DCA concentration was observed post day 7 samplings. Production of volatile radiocarbon labelled carbon dioxide was observed. Generation of polar fulvic acid associated products were the result of DCA degradation.

VII. Reviewer's Comments:

1) The study is not acceptable at this time to fulfill the requirement for aerobic aquatic metabolism data. It will become acceptable when certain inconsistencies (discussed below) are resolved.

   It provides the supplementary information that aerobic metabolism in "active" water and sediment is rapid with a half-life of 2 days under experimental conditions.

2) The production of DCA in the "sterile" system is at variance with the observations made in the hydrolysis and aqueous photolysis studies, where no such production occurred. These results could be explained if the "sterile" system regained some microbial activity during the course of the incubation. This seems to be ruled out by the plates which indicated no activity.



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3) The behavior of DCA in the sterile and vital systems also seems to be inconsistent, since DCA apparently remains in the water in the sterile system while becoming bound to the soil in the vital system.

4) The applicant must provide a revised description of the extraction of bound material (on page 16 of the current submission), since the actual procedure used cannot be discerned from the material submitted. In addition to a narrative description, a flow chart or diagram will also be appreciated.

VIII. CBI Information Addendum: attached

RIN 1876-95

PROPANIL EFGWB REVIEW

Page_____ is not included in this copy.

Pages 58 through 74 are not included.

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____ Identity of product impurities.

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____ Description of quality control procedures.

____ Identity of the source of product ingredients.

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____ The product confidential statement of formula.

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✓ FIFRA registration data.

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| |
|---|
| Environmental Fate & Effects Division<br>PESTICIDE ENVIRONMENTAL FATE ONE LINE SUMMARY<br>**PROPANIL**<br>Last Update on November 7, 1991<br>[V] = Validated Study [S] = Supplemental Study [U] = USDA Data |

| LOGOUT | Reviewer: | Section Head: | Date: NOV 15 1991 |
|---|---|---|---|

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

Empirical Form: $C_9H_9Cl_2NO$
Molecular Wgt.: 218.08 Vapor Pressure: 4.00E -5 Torr
Melting Point : °C Boiling Point: °C
Log Kow : 2.28 pKa: @ °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 | @ °C | |
| Acetonitrile | E | ppm | @ °C | |
| Benzene | E | ppm | @ °C | |
| Chloroform | E | ppm | @ °C | |
| Ethanol | E | ppm | @ °C | |
| Methanol | E | ppm | @ °C | |
| Toluene | E | ppm | @ °C | |
| Xylene | E | ppm | @ °C | |
| | E | ppm | @ °C | |
| | E | ppm | @ °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 :



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Environmental Fate & Effects Division
PESTICIDE ENVIRONMENTAL FATE ONE LINE SUMMARY
**PROPANIL**
Last Update on November 7, 1991
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Photolysis (161-2, -3, -4)
[S] Water:STABLE FOR 30 DAYS MRID 410707-01
[ ] :
[ ] :
[ ] :

[ ] Soil :
[ ] Air :

Aerobic Soil Metabolism (162-1)
[S] 2 DAYS
[ ]
[ ]
[ ]
[ ]
[ ]
[ ]

Anaerobic Soil Metabolism (162-2)
[S] 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)
[S] HALF-LIFE 2-3 DAYS IN RICE PADDY WATER AND SEDIMENT
[ ] MRID 418726-01
[ ]
[ ]
[ ]
[ ]
[ ]

Aerobic Aquatic Metabolism (162-4)
[S] HALF-LIFE 2 DAYS IN RICE PADDY WATER AND SEDIMENT
[ ] MRID 418487-01
[ ]
[ ]
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[ ]



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Environmental Fate & Effects Division
PESTICIDE ENVIRONMENTAL FATE ONE LINE SUMMARY
**PROPANIL**
Last Update on November 7, 1991
[V] = Validated Study   [S] = Supplemental Study   [U] = USDA Data

Soil Partition Coefficient (Kd) (163-1)
[ ]
[ ]
[ ]
[ ]
[ ]
[ ]

Soil Rf Factors (163-1)
[ ]
[ ]
[ ]
[ ]
[ ]
[ ]

Laboratory Volatility (163-2)
[ ]
[ ]

Field Volatility (163-3)
[ ]
[ ]

Terrestrial Field Dissipation (164-1)
[ ]
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Aquatic Dissipation (164-2)
[ ]
[ ]
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[ ]

Forestry Dissipation (164-3)
[ ]
[ ]



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Environmental Fate & Effects Division
PESTICIDE ENVIRONMENTAL FATE ONE LINE SUMMARY
**PROPANIL**
Last Update on November 7, 1991
[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)
[ ]
[ ]
[ ]

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)
$CO_2$
3,3',4,4'-tetrachloroazobenzene (TCAB)



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



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