

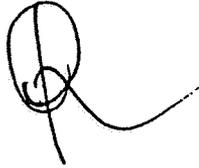
US EPA ARCHIVE DOCUMENT

Shaughnessy No.: 081901

Date out of EAB: OCT 30 1987

To: Lois Rossi
Product Manager 21
Registration Division (TS 767C)

From: Emil Regelman, Supervisory Chemist
Review Section #3
Exposure Assessment Branch
Hazard Evaluation Division (TS 769C)



Attached, please find the EAB review of...

Reg./File # 50534-7

Chemical Name: chlorothalonil 2,4,5,6-tetrachloroisophthalonitrile

Type Product: fungicide

Product Name: n.a.

Company Name: Fermenta Plant Protection Co.

Purpose: response to Registration Standard data requirement

Date Received: 6/17/87 Action Code: 660

Date Completed: OCT 30 1987 EAB # (s): 70754

Monitoring Study Requested: _____ Total Reviewing Time: 3.0 days

Monitoring Study Volunteered: _____

Deferrals to: _____ Ecological Effects Branch

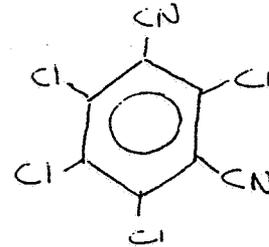
_____ Residue Chemistry Branch

_____ Toxicology Branch

1. CHEMICAL:

chemical name: 2,4,5,6-tetrachloroisophthalonitrile
common name: chlorothalonil
trade name:
structure: See also Table 1 (attached) for degradates

CAS #: 1897-45-6
Shaughnessy #: 081901



2. TEST MATERIAL: described below

3. STUDY/ACTION TYPE: data submission in response to Registration Standard

4. STUDY IDENTIFICATION:

Nelson, T.R. An Aqueous Photolysis Study with ¹⁴C 2,4,5,6-tetrachloroisophthalonitrile (Chlorothalonil), SDS-2787. performed by Ricerca, Inc., Painesville, OH. sponsored by Fermenta Plant Protection Company, Painesville, OH. [reviewer's note: these appear to be part of the same corporate entity which used to be Diamond Shamrock.] dated 4/10/87. rec'd EPA 5/4/87. EPA Acc.# 401834-18.

5. REVIEWED BY:

Typed Name: E. Brinson Conerly
Title: Chemist, Review Section 3
Organization: EAB/HED/OPP

E. Brinson Conerly 10/29/87

6. APPROVED BY:

Typed Name: Emil Regelman
Title: Supervisory Chemist, Review Section 3
Organization: EAB/HED/OPP

OCT 30 1987

Emil Regelman

7. CONCLUSIONS:

The data presented in this study indicate that chlorothalonil is relatively stable to photodegradation (estimated $t_{1/2}$ ca. 65 days). However, additional information will be required to satisfy Guidelines requirements.

Examination of the EAB file indicates that the remaining data requirements are as follows, as of the most recent prior review (ADA 5/15/87).

- 1) aqueous photolysis -- discussed in this review; may be made acceptable by provision of satisfactory additional information
- 2) soil photolysis
- 3) field rotational crops

A study may be required on aerobic aquatic metabolism, based on results of specialized aquatic use studies now in progress (per ADA 5/15/87).

Data requirements which have been fulfilled include the following:

- 1) hydrolysis -- per registration standard [Dynamac T1/T2, 5/7/84]

compound is stable for up to 72 days at pH 5 and 7, and has a $t_{1/2}$ of 33-43 days at pH 9 and 0.5 ppm, and 28-72 days at pH 9 and 1.5 ppm. [Note that the aqueous photolysis study reviewed herein states that the solubility limit in H₂O is 0.5 ppm.]

2) aerobic soil metabolism -- fulfilled per registration standard

[¹⁴C] chlorothalonil is degraded with half-lives of <1-16, 8-31, and 7-16 days in nonsterile aerobic sandy loam, silt loam and peat loam soils, respectively at ca. 77-95 F and 80% of field moisture capacity. When chlorothalonil (WP) was applied to nonsterile soils ranging in texture from sand to silty clay loam, at 76-100 F and 6% soil moisture, it was degraded with half-lives of 4 to >40 days. Increasing either soil moisture content (0.6 - 8.9%) or incubation temperature (76 - 100 F) enhanced chlorothalonil degradation. Soil pH (6.5-8) does not appear to influence or only negligibly influence the degradation rate of chlorothalonil; however, soil sterilization greatly reduced the degradation rate. The major degradate identified in non-sterile aerobic soil was DAC-3701 representing up to ca. 69% of the applied radioactivity. Other identified degradates included DS-19921, trichloro-3-carboxybenzamide, 3-cyanotrichloro-hydroxybenzamide, and 3-cyanotrichlorobenzamide.

3) anaerobic soil metabolism -- per review of HLB 4/22/86

The anaerobic aquatic metabolism study was accepted in lieu of this study.

4) anaerobic aquatic metabolism -- per review of HLB 4/22/86

The half-life of chlorothalonil in flooded sandy loam or silt loam soils is expected to be about 5-15 days. Degradates will include 4-hydroxy-2,5,6-trichloroisophthalonitrile; 3-cyano-2,4,5,6-tetrachlorobenzamide; 2-hydroxy-5-cyano-3,4,6-trichlorobenzamide; and 3-carboxy-2,5,6-trichlorobenzamide. Only a minute fraction of the residues are expected to volatilize in anaerobic aquatic environments.

5) leaching, adsorption/desorption -- per HLB review 8/1/86

Unaged chlorothalonil is only slightly mobile in silty clay, silt, and sandy soil as shown by Freundlich k_{ads} values of 26, 29, and 20, respectively. Less than 4% of the adsorbed pesticide was desorbed from silty clay loam and less than 7% from the silty soil upon each of two dilutions. In contrast, the Freundlich k_{ads} value for sand soil was shown to be 3, and up to about 28% was desorbed upon dilution, indicating a fairly high mobility in sand.

Aged residues of chlorothalonil as judged by column leaching studies are slightly mobile in sandy loam, silt loam, and clay loam soils and mobile in sand soils. The degradates 3-carboxy-2,5,6-trichlorobenzamide (SDS-46851), 2-hydroxy-5-cyano-3,4,6-trichlorobenzamide (SDS-47525), and 4-hydroxy-2,5,6-trichloroisophthalonitrile (SDS-3701) are mobile in all four soils; 3-cyano-2,5,6- and 3-cyano-2,4,5-trichlorobenzamide are mobile in sandy loam, silt loam, and sand soils.

6) confined rotational crops -- per the registration standard

Uptake occurs in lettuce, green beans, and carrots. Field studies required.

- 7) fish bioaccumulation -- per previous review (ADA 5/15/87)
Data may be required depending on K_{OW} .

Certain data requirements have been waived:

- 1) photolysis in air
- 2) laboratory volatility
- 3) field volatility

Other data requirements are not being imposed at this time.

8. RECOMMENDATIONS:

Note that a prompt response to this request for further information may permit the inclusion of the study in the FRSTR as a data requirement fulfilled. The applicant should provide clarification on the following points:

- 1) absorbance spectrum of the parent compound in water vs. in ethanol.
- 2) exposure intervals --
Why was exposure not done on June 21 or 22? We note that this period was a weekend.
Was exposure continuous on June 23-24 and 24-27, or if not, what were the actual intervals?
- 3) light source --
Do the applicants believe that this was a more severe test of photolability than exposure to natural sunlight would be, and, if so, can they provide justification for this position?

9. BACKGROUND:

This is information submitted in response to a registration standard. Clarifying statements discussed above may demonstrate that repeating the study using Guideline conditions would not provide any additional useful information. Note that the FRSTR for this chemical is scheduled for completion in early 1988. The hydrolysis study which was accepted previously is somewhat suspect, especially at pH 9.

10. DISCUSSION OF INDIVIDUAL TESTS OR STUDIES:

A. STUDY IDENTIFICATION:

Nelson, T.R. An Aqueous Photolysis Study with ^{14}C 2,4,5,6-tetrachloroisophthalonitrile (Chlorothalonil), SDS-2787. performed by Ricerca, Inc., Painesville, OH. sponsored by Fermenta Plant Protection Company, Painesville, OH. [reviewer's note: these appear to be parts of the same corporate entity which used to be Diamond Shamrock.] dated 4/10/87. rec'd EPA 5/4/87. EPA Acc. # 401834-18.

B. MATERIALS AND METHODS:

test substance -- ^{14}C chlorothalonil, uniformly ring-labelled purity 99.0%,
spec. act. 78.74 mci/mm (662,000 dpm/ug)
stock solutions -- in dichloromethane (DCM)
above radiolabelled compound @ 1.3038×10^6 dpm/ul [1 ul=1.96ug] 1 ug/ml

4
153

unlabelled analytical standard grade chlorothalonil
test solution -- mixture of stock solutions @ 200,305 dpm/ug [250 ug A.S. + 55
ul radiolabelled compound]. DCM is allowed to evaporate, and the residue
dissolved in 1 L of H₂O, stirred overnight, and filtered. The resulting
solution is 0.33 ppm [compared to 0.5 ppm solubility] by LSC. 414.6 gm
solution is placed in the photolysis vessel, and 404.8 gm in the control
Al-foil wrapped vessel.

light source -- GE type RS -- UV spectrum attached, Pyrex filtered light
intensity ca. 3.3x the measured intensity of sunlight on June 11, 1986,
which was a clear, bright day (per applicant).

exposure protocol -- a total of 118 hours over 11 calendar days as follows:

June 17, 1986 -- 5.0 hrs
June 18, 1986 -- 5.5 hrs
June 19, 1986 -- 6.0 hrs
June 20, 1986 -- 5.0 hrs
June 21, 1986 -- 0.0 hrs
June 22, 1986 -- 0.0 hrs
June 23, 24, 1986 -- 28.5 hrs
June 24, 25, 26, 27, 1986 -- 68.0 hrs

temperature -- 25°C

samples -- exposure vessel sampled @ 0, 5, 10.5, 21.5, 50, and 118 hrs exposure.

control -- control vessel sampled @ 0, 5, 10.5, 21.5, 50, and 118 hrs exposure.

analytical method

total radioactivity was determined by LSC

parent and degradates were quantified by the following scheme:

- 1) the aqueous solution was made acidic (pH < 2) and partitioned
3x with ca. 50 ml diethyl ether (DEE).
- 2) Combined DEE extracts and aqueous extracts were analyzed for
radioactivity by LSC.
- 3) The DEE extracts were dried in vacuo, taken up in MeOH, trans-
ferred, dried again by air flow, taken up in H₂O, and analyzed
by HPLC by a gradient system known to separate the 5 identified
metabolites and parent.

C. REPORTED RESULTS:

No real change occurred in the foil-wrapped samples during the study. No
loss occurred due to volatility from the photolysis samples over the course
of the study. The amount of radiolabel in the aqueous extract increased
to a high of 15.7% at the last exposure time (118 hours). The major degradate
was identified as SDS-3701. The remaining degradate(s) apparently comprised
a complex mixture of highly polar compounds which were not further identified,
but could not individually amount to 10% of the parent.

D. STUDY AUTHOR'S CONCLUSIONS/QUALITY ASSURANCE MEASURES:

"The results of this study indicate that chlorothalonil dissolved in water
is labile to photolysis; however, the rate of photolysis is slow ($t_{1/2}$ =
64.7 12-hour sunlight days). The products of the photolysis include SDS-
3701, 1 minor diethyl ether soluble (<5%) component, a complex mixture of
ethyl acetate soluble components none of which could approach 10% of the
total, and an aqueous soluble pool amounting to at most (.443 x 15.7) 7.5%
of the total. It is also clear that chlorothalonil did not volatilize
nor form volatile components during ... exposure to UV light at 25° C."

E. REVIEWER'S DISCUSSION AND INTERPRETATION OF STUDY RESULTS:

- 1) The light absorption spectrum of chlorothalonil in ethanol indicates absorption in the UV range (a major peak at ca. 230 nm) and at 310 - 330 nm (two apparent minor peaks). However, it must be noted that the light absorption spectrum of chlorothalonil which is reported here was done in ethanol, rather than water -- the absorption in water may be different.

With the foregoing caveat, the following comments apply:

- a) The light source does not closely simulate the spectrum of natural sunlight over the range reported.
 - b) Only a very narrow portion of the spectrum is reported at all.
- but
- c) The applied light was of greater intensity than summer sunlight.
 - d) The wavelength of the light applied was that of maximum expected absorbance.

It appears that this photolysis may have been done under conditions more favorable to photodegradation than exposure to natural light would be. Further clarification is needed.

- 2) Although a half-life has been derived from the data produced in this study, it is at best an indication, rather than a "hard number". We can state from these results that photolysis in water does not appear to be a major route of degradation for this compound.
- 3) Exposure intervals are presented unclearly, and no rationale is given for what appears to be a somewhat random exposure scheme. Clarification is needed.

The following are comments and observations, not objections.

- 4) The test solution was unbuffered, but was measured throughout the study at ca. pH 7, where the material appears to be stable. Further, the dark control showed no change in chlorothalonil content.
- 5) The major photoproduct is the 4-hydroxy analog, reaching a maximum of ca. 10% over the study period.
- 6) The experiment was done at a concentration greater than half the stated solubility limit in water of 0.5 ppm.
- 7) Material balances throughout the study are acceptable.
- 8) The included protocol calls for photolysis in pH 5 buffer. No explanation for deviating from this protocol is given. However, hydrolysis results indicate that the compound is probably stable at either pH, and this deviation should not alter the results. The applicant should clarify for the record.

11. COMPLETION OF ONE-LINER: not amended

12. CBI APPENDIX: included

6
~~2~~

RIN 8587-93

EPA Reg II 50532-7

Page ___ is not included in this copy.

Pages 7 through 11 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.
