Shaughnessy Number: 081901

Date out of EFGWB: 2/10/93

To: S. Lewis
Product Manager 23
Registration Division (H7505C)

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)

Attached, please find the EFGWB review of...

Reg./File #: 050534-00008

Chemical Name: Chlorothalonil

Type Product: fungicide

Product Name: Bravo 500

Company Name: ISK Biotech

Purpose: various

Date Received: 7/23/92

Action Code: ____ EFGWB #(s): 92-0489, -0491, -0576, -0616, -0631, -0782, -0788

Total Review Time: __ days

EFGWB Guideline/MRID/Status Summary Table: The review in this package contains...

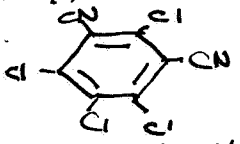
161-1		162-4	MRID# 422261-01	164-4		166-1	
161-2		163-1		164-5		166-2	
161-3		163-2		165-1		166-3	
161-4		163-3		165-2		167-1	
162-1		164-1		165-3		167-2	
162-2		164-2		165-4		201-1	
162-3		164-3		165-5		202-1	

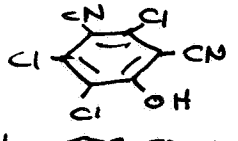
Y = Acceptable (Study satisfied the Guideline)/Concur
P = Partial (Study partially satisfied the Guideline, but additional information is still needed)
S = Supplemental (Study provided useful information, but Guideline was not satisfied)
N = Unacceptable (Study was rejected)/Non-Concur

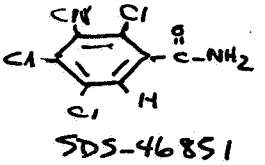
bcp

1. CHEMICAL:

chemical name: 2,4,5,6-tetrachloro-1,3-benzenedicarbonitrile
common name: Chlorothalonil
trade name: Bravo, Clortosip, Daconil 3787, Exotherm Termil.
structure:


Chlorothalonil


SDS-3701


SDS-46851

CAS #:
Shaughnessy #: 081901

2. TEST MATERIAL: described in DERs

3. STUDY/ACTION TYPE:

EFGWB 92-0489 -- add use on passion fruit

EFGWB 92-0491 -- add use on passion fruit (duplicate of 92-0489)

EFGWB 92-0576 -- submission of aerobic aquatic metabolism study, MRID# 422261-01

EFGWB 92-0616 -- request for clarification of status of data requirements for photodegradation in water and on soil

EFGWB 92-0631
1) request for removal of rotational crop restriction imposed because of SDS-46851 and SDS-3701
2) submission of summary of environmental fate data
3) waiver of requirement for data on accumulation in rotated crops

EFGWB 92-0782 -- submission of study on residues in turf clippings, MRID#s 422220-01, -02, -03

EFGWB 92-0788 -- add use on cherries

4. STUDY IDENTIFICATION:

Hatzenbeler, C.J. An Aerobic Aquatic Soil Metabolism Study with ^{14}C-Chlorothalonil, performed by Ricerca, Inc, Painesville, OH, sponsored by ISK Biotech, Mentor, OH. dated 8/19/91, rec'd 2/27/92, MRID# 422261-01.

King, C., Ballee, D.L., and Marks, A.F. Residues of Tetrachloroisophthalonitrile (Chlorothalonil, SDS-2787) on Turf Clippings - 1985. performed by Ricerca, Inc. Painesville, OH, sponsored by Fermenta Plant Protection Company, Painesville, OH. rec'd 2/27/92, MRID# 422220-01.

King, C., and Ballee, D.L. Residues of 4-Hydroxy-2,5,6 trichloroisophthalonitrile (Chlorothalonil, SDS-2787) on Turf Clippings - 1985. performed by Ricerca, Inc. Painesville, OH, sponsored by Fermenta Plant Protection Company, Painesville, OH. rec'd 2/27/92, MRID# 422220-02.

bcp

Cassidy, P.S., Dillon, K.A., and Ballee, D.L. Residues of Tetrachloroisophthalonitrile (Chlorothalonil, SDS-2787), SDS-3701, SDS-46851, HCB, and PCBN on Turf Clippings - 1985. performed by Ricerca, Inc. Painesville, OH, sponsored by Fermenta Plant Protection Company, Painesville, OH. rec'd 2/27/92, MRID# 422220-03.

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

E. B. Conerly-Perks
2/8/93

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

Akiva Abramovitch
2/8/93

7. CONCLUSIONS:

EFGWB 92-0489, EFGWB 92-0491 -- Added use on passion fruit

There are no data in these submissions. The applicant cites residue data submitted under MRID# 420590-01 to support this use. If there are no objections from Dietary Exposure or Toxicology Branch, EFGWB has no objections to adding this use.

EFGWB 92-0576 -- aerobic aquatic metabolism data, MRID# 422261-01

The study is acceptable to fulfill the requirement for data on aquatic aerobic metabolism. Chlorothalonil is rapidly metabolized (first $t_{\frac{1}{2}}$ = ca. 1 - 2 hr) and none of the identified degradates appeared to persist. During the first few hours after dosing, soil bound material increased to a maximum of ca. 58% at 6 hours, and, after that, approximately 30-35% of applied material was bound to soil throughout the experimental period. The semilog plot of time vs concentration was not linear, and the mechanisms which were occurring are not clear.

EFGWB 92-0616 -- request for clarification of status of data requirements for photodegradation in water and on soil

The applicant has submitted copies of EPA letters and reviews indicating that EFGWB accepted marginally satisfactory studies to fulfill aqueous and soil photolysis data requirements.

EFGWB 92-0631

1) request for removal of rotational crop restriction imposed because of SDS-46851 and SDS-3701 -- The request for removal of rotational crop restriction was granted in an EFGWB review dated 5/1/92.

2) request for waiver of the requirement for data on accumulation in irrigated crops -- The request is based on the aerobic aquatic metabolism reviewed in this document, and an aquatic field run-off

study (MRID#s 00137146 and 00127862). The aquatic metabolism study indicates a short first "half-life" of 1-2 hours, and supports the applicant's position. The aquatic field run-off study has apparently not been reviewed by EFGWB. Accordingly, EFGWB will not waive the requirement at this time, but will hold it reserved until the study is submitted and evaluated.

EFGWB 92-0782 -- study on residues in turf clippings, MRID# 422220-01, -02, 03

EFGWB recognizes that these were not submitted as turf dissipation studies. None would be acceptable as such, since it is impossibile to confirm the application rate and because there are no data on residues in compartments other than the top parts of the grass. They are not discussed in detail in this review, but only summarized.

The submitted data are intended to show that, <u>using practices common to golf course greens</u>, Chlorothalonil residues do not accumulate on the grass and therefore do not threaten wild life (e.g. Canada geese). Mowing and removal of clippings was done daily. The registrant makes the implicit assumption that the top part of the grass intercepts all or most of the chemical and therefore represents the exposure risk to humans and/or wildlife. However, there is no specific information in the study to demonstrate that the assumption is true, e.g. analyses of soil or water. The data do appear to be consistent with lack of accumulation in the grass, since concentrations in the clippings do decrease. Because of the specialized regimen, the apparently rapid decline of the parent, degradates, and manufacturing impurities is most probably completely explained by the physical removal (by mowing) of the portion of the grass which intercepted the application. <u>This rapid disappearance may not occur elsewhere</u>. <u>If mowing and clipping removal are carefully done</u>, this <u>might</u> be effective in mitigating exposure, However, exposure could occur through some means other than the grass, and the submitted material does not provide any means of assessing these possibilities. The 1991 study appears to be similar information, with data on additional analytes.

EFGWB 92-0788 -- add use on cherries

8. <u>RECOMMENDATIONS</u>:

The unfulfilled data requirements are significant and should be fulfilled as soon as possible. These include aerobic soil metabolism, field dissipation (partial), and fish bioaccumulation. Note that ground water vulnerability is still a concern *[A protocol for the ground water monitoring study was recently reviewed and found unacceptable]*. The referenced aquatic field run-off study should be forwarded to EFGWB for evaluation.

EFGWB 92-0489, EFGWB 92-0491 -- added use on passion fruit

This appears to be a minor use. Given that assumption, if there are no objections from Dietary Exposure or Toxicology Branch, then EFGWB has none. The applicant should be so informed.

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EFGWB 92-0576 -- aerobic aquatic metabolism data, MRID# 422261-01

The applicant should be informed that the study is acceptable to fulfill the requirement for data on aquatic aerobic metabolism.

EFGWB 92-0616 -- request for clarification of status of data requirements for photodegradation in water and on soil

The applicant is correct that studies were accepted to fulfill these data requirements. No more data need be submitted.

EFGWB 92-0631

1) request for removal of rotational crop restrictions imposed because of SDS-46851 and SDS-3701, summary of environmental fate data. This was granted in a review dated 5/1/92.

2) request for waiver of requirement for data on accumulation in irrigated crops. This requirement is reserved until receipt and evaluation of the aquatic field run-off study the applicant has cited (MRID#s 00137146 and 00127862).

EFGWB 92-0782 -- study on residues in turf clippings, MRID# 422220-01, -02, 03

The applicant should be informed that the studies did not demonstrate definitively that mowing and clipping removal will be sufficient to insure that wildlife is not exposed to Chlorothalonil on treated grass. However, the data do not disprove the possibility that the practice could be protective. The studies were not submitted as EFGWB turf field dissipation studies, and would not be acceptable as such, due to the impossibility of confirming the application rate and to the lack of data on residues in compartments other than the top parts of the grass.

EFGWB 92-0788 -- add use on cherries

The potential magnitude of this use is not known, and some cherry-growing areas may be vulnerable to ground water contamination. Given these uncertainties, EFGWB is unable to recommend approval for this added use at this time.

9. BACKGROUND:

DATA BASE ASSESSMENT

Although the data base is far from complete and some data are only partially acceptable, there is some available information about environmental fate of Chlorothalonil. The available data suggest a relatively non-persistent compound based on its susceptibility to metabolism, although unacceptable field studies suggest half-lives of as much as 60 days. An unacceptable study suggests that it accumulates moderately in fish. It has been detected in rotational crops following

treatment at an exaggerated rate. Mobility data are equivocal; additional data which are in process may serve to clarify this issue. The degradate DAC [SDS] 3701 (4-OH-2,5,6-trichloroisophthalonitrile) has been detected in ground water, and is suspected of leaching.

DEGRADATION

Chlorothalonil is stable to hydrolysis, aqueous photolysis and soil photolysis, and is susceptible to anaerobic aquatic metabolism ($t_{\frac{1}{2}}$ 5 - 15 days) and aerobic aquatic metabolism (first $t_{\frac{1}{2}}$ ca. 1 - 2 hr).

MOBILITY

Lab studies indicate low leachability of parent compound in most soils. However, the finding of Chlorothalonil degradates in ground water has triggered monitoring and small scale prospective data requirements. Protocols for these studies have been reviewed recently and found unacceptable, They must be resubmitted.

DISSIPATION

Submitted terrestrial field dissipation studies have been unacceptable and are inconclusive. Available data suggest half-lives ranging from 15 to 60 days.

ACCUMULATION

Confined rotational crops following treatment at an exaggerated rate (4X) showed some uptake of radioactivity, only ca. 1/3 of which was recognizable as Chlorothalonil-related. At the recommended label rate, these residues would be undetectable. A field crop accumulation study *of supplemental quality* showed no uptake. Unacceptable data suggest that accumulation in fish is moderate (ca. 75 - 550 X).

The data requirements are summarized below.

Hydrolysis -- fulfilled -- MRID # 00405-39 -- stable at pH 5 and 7; 10% degrades in 30 days at pH 9; 2,4,5,6-tetra-Cl-isophthalimide was the only degradate

Aqueous Photolysis -- fulfilled -- MRID#s 000872-81, 401834-18, 000405-40, 1988 Reg. Std. -- indicates stability to photolysis

Soil Photolysis -- fulfilled -- (MRID# 001437-51, 1988 Reg. Std.) -- indicates stability to photolysis

Aerobic Soil Metabolism -- <u>not fulfilled</u> -- the study (per Guidelines subpart N) must establish patterns of disappearance of parent; appearance and disappearance of degradates; identity of degradates

Anaerobic Soil Metabolism -- fulfilled by acceptable anaerobic aquatic metabolism study *[which has an $t_{\frac{1}{2}}$ of 5-15 days]* (10/23/85, also HLB 4/22/86, MRID# 0014790-75)

Anaerobic Aquatic Metabolism -- fulfilled -- (10/23/85, HLB 4/22/86, MRID# 001479-75) -- $t_{\frac{1}{2}}$ 5-15 days

Aerobic Aquatic Metabolism -- fulfilled -- (this review, MRID# 422261 -01) first $t_{\frac{1}{2}}$ = 1.04 hr for salt water, 1.40 hr for fresh -- see the attached DER for details.

Leaching/Adsorption/Desorption -- fulfilled (8/1/86, MRID#s 001151-05, -001537-10) -- low leachability in lab, but findings of degradates in ground water triggered monitoring requirements. k_{ads} = 3 (sand) to 29 (silt) in batch studies.

Terrestrial Field Dissipation -- partially fulfilled (MRID # 00087296, 1984 Reg. Std.). In that study, Chlorothalonil had a half-life of 1-2 months in sandy loam soil, and did not appear to leach. Other studies which have been reviewed are:

Fresno, CA -- MRID# 415648-29. This study is unacceptable for several reasons listed below. These data are considered to be of uncertain value and should not be used to predict the environmental behavior of chlorothalonil and its degradates. **These data do not serve to define a pattern or time course for the dissipation of chlorothalonil under field conditions. Soil sampling may not have gone deep enough to define the extent of leaching of chlorothalonil and its degradates.** Analyses were done on composited samples (and sampling variation thereby minimized), and therefore, EFGWB cannot assess the "inherent" precision and accuracy of the procedures. The study author reported a half-life of 58 days for chlorothalonil in the upper 12 inches of soil using **selected** data, but since values were arbitrarily discarded, the calculated half-life is considered to be of questionable validity.

Donalsonville, GA -- MRID# 451648-28. The study is unacceptable. **The data do not serve to define a pattern or time-course for the dissipation of chlorothalonil under field conditions because they are too randomly variable. Soil was only sampled through day 29 following the tenth application, except for samples taken at 222 days posttreatment. The depth of soil sampling was insufficient to define the extent of leaching of chlorothalonil and its degradates.** Chlorothalonil was detected to a depth of 12-inches. It dissipated with an observed half-life of 14-29 days from the upper 12 inches of a plot of sandy loam soil that was treated at 10-day intervals with chlorothalonil (Bravo 720, 6 lb/gal FlC) at 1.12 lb ai/A/application ten times (total 11.2 lb ai/A). The degradates were 4-hydroxy-2,5,6-trichloroisophthalo nitrile (SDS-3701), 2-hydroxy-5-cyano-3,4,6-trichlorobenzamide (SDS-47525), 3-carboxy-2,5,6-trichlorobenzamide (SDS-46851), 3-cyano-2,4,5-trichlorobenzamide (SDS-47523/SDS-47524), 3-cyano-2,4,5,6-tetrachlorobenzamide (SDS-19221). The manufacturing impurities HCB and PCNB were isolated as deep as the 9- to 12-inch depth. Per the authors PCBN levels were related to the level of chlorothalonil residues present, but the levels of HCB were not. In addition, pretreatment samples taken from the two treated plots contained detectable residues of HCB (0.003-0.006 ppm).

Greenfield, CA -- MRID# 415648-30. This study is unacceptable. **The cultural practices employed during the course of the study compromised study results.** It is highly probable that these practices (cultivation, disking, and chiseling) resulted in movement of chlorothalonil residues to lower soil depths. Because the surface soil layers were mixed during the course of the study, the concentration of pesticide may have been diluted by bringing pesticide-free soil from lower horizons, and may have increased the rate of dissipation by aerating the soil and presenting

new nutrient sources to the microbial population. Study results may also have been compromised by soil sampling procedures used -- samples may have been contaminated by the sampling process itself. Soil was not sampled deeply enough to define the extent of leaching of chlorothalonil and its degradates. At both treated plots, chlorothalonil residues were detected in the 12- to 15-inch depth, the lowest soil depth sampled. The soil should have been sampled to depths (preferably two sampling depths) at which residues were nondetectable. From selected data, the study author calculated a half-life of 40 days for chlorothalonil. The arbitrary exclusion of data used to calculate the half-life causes the resulting half-life to be of questionable value.

Accumulation in Confined Rotational Crop -- MRID # 410302-11 -- lettuce, carrots, and wheat grown as confined rotational crops. Some uptake and concentration were detected at an exaggerated rate of application (4 x the maximum single application). Closely related metabolites accounted for ca. 1/3 of total radioactivity observed in the plants. Remaining labelled material may derive from the soil "carbon pool".

Accumulation in Field Rotational Crops -- partially fulfilled (Kenyon and Ballee, no MRID#. This field crop accumulation study is not acceptable to completely fulfill the data requirement because the soil was not analyzed at planting time. Therefore, it is not certain that residues were available for uptake, or at what level. For these reasons, the study can only be considered supplemental. Under these experimental conditions, no uptake was observed.

Previously reviewed MRID#s 415648-32 through -46 cannot be used to fulfill data requirements at this time because the data were not presented in a reviewable format. In order for this study to be reevaluated, the registrant must provide summarized soil residue data, complete site characteristics, and meteorological data. In addition, the lengths of time the samples were stored frozen and acceptable freezer storage stability data must be provided. An ancillary Study - Freezer Storage Stability -- MRID#s 415648-20 through -27 cannot be used to fulfill data requirements because the experimental design used was not appropriate for determining the freezer storage stability of chlorothalonil and its degradates in the various plant matrices.

Laboratory Accumulation - Fish -- not satisfied by MRIDs 00086629, 00029411, and 00086630 taken together; a new study is required. The original report (Dynamac, December 12, 1983) and the review of 11/29/92 were reexamined for this review, and an error has been corrected.[1] A copy of the review of 11/29/92 is attached.

10. DISCUSSION OF INDIVIDUAL TESTS OR STUDIES: n.a.

11. COMPLETION OF ONE-LINER: attached

12. CBI APPENDIX: attached to DERs

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[1] Several previous reviews reported fish bioaccumulation data incorrectly.

DATA EVALUATION REVIEW 1

I. Study Type: aerobic aquatic metabolism, Guideline 163-4

II. Citation:

Hatzenbeler, C.J. An Aerobic Aquatic Soil Metabolism Study with ^{14}C-Chlorothalonil, performed by Ricerca, Inc, Painesville, OH, sponsored by ISK Biotech, Mentor, OH. dated 8/19/91, received at EPA 2/27/92 under MRID# 422261-01.

III. Reviewer

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

E.B. Conerly-Perks
12/15/92

IV. Conclusions:

The study is acceptable to fulfill the requirement for data on aquatic aerobic metabolism. Based on these data, it can be stated that Chlorothalonil is rapidly metabolized and none of the identified degradates appeared to persist. The investigators reported a first half-life of 1-2 hours. It should be noted that the semilog plot of time vs. concentration is not linear. The process being observed is therefore not pseudo-first-order. The initial disappearance of parent may be due to binding alone, with metabolism following at a somewhat slower rate. During the first few hours after dosing, soil bound material increased to a maximum of ca. 58% at 6 hours, and after that approximately 30-35% of applied material was bound to soil throughout the experimental period.

V. Materials and Methods

ABSTRACT

The aerobic metabolism of Chlorothalonil in salt water/sediment and in fresh water/sediment was studied at 25°C using ^{14}C-Chlorothalonil at 0.6 ppm in a system which consisted of water/sediment at a 9:1 ratio.

Chlorothalonil is rapidly metabolized under aerobic aquatic conditions in both salt water and fresh water systems containing sediment. At 25°C, the calculated initial half-life of Chlorothalonil both in salt water/sediment and in fresh water/sediment was less than two hours. The major metabolites were 5-cyano-4,6,7-trichloro-2H-1,2-benzisothiazol-3-one (SDS-67042) and its sulfoxide. The minor metabolites identified both in salt water and in fresh water sediments are 2,5,6-trichloro-4-(glutathion-S-yl)isophthalonitrile (SDS-66382); 2,5-dichlor-4,6-di(glutathion-S-yl)isophthalonitrile (SDS-66432); 2,5,6-trichloro-4-(thio)isophthalonitrile (SDS-13353); and 2,5,6-trichloro-4-hydroxyisophthalonitrile (SDS-3701). The major metabolites reached peak concentrations by nine days and then declined as they gradually underwent further degradation leading to increased levels of polar degradates and nonextractable residues.

MATERIALS

test compound -- U(ring)-^{14}C-Chlorothalonil, purity >97.0%, spec. act. 33,209 dpm/μg; dosing solution 0.5 mg Chlorothalonil/ml

test standards -- information attached

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test system

salt water/sediment -- silty loam sediment from Chesapeake Bay; water - deionized water mixed with proprietary saline mix

fresh water/sediment -- silty loam sediment from Grand River (Painesville, OH), classified as silty loam; deionized water

METHODS

procedure

salt water

3 foil-wrapped flasks, 50 gm each of test sediment and H_2O q.s. 450 ml, were preincubated 3 days at 25 ± 1 °C under constant agitation. pH and dissolved oxygen were monitored periodically, and water was added to compensate for evaporation losses, and pH was maintained at 8.33 ± 0.04 (the initial pH of the salt water/sediment system. After 3 days, two flasks were dosed with 0.3 mg ^{14}C-Chlorothalonil and the third retained as control. Samples were removed for analysis at 0, 1, 3, 6, 12, 24, and 72 hours, 9, 16, 23, and 30 days.

fresh water

as described above, but pH WAS 7.02 ± 0.04

extraction

The sediment following centrifugation was extracted 3x with acetone /H_2O /HCl. The three extracts were combined and radioactivity determined by LSC. Certain samples of extracted solids were subjected to acid hydrolysis (6 N HCl at 100°C for at least 18 hours). The acid hydrolysate was filtered, pH adjusted and partitioned against EtOAc.

The water portion was decanted into an equal volume of acetone/ H_2O/ HCl (89/10/1), and the radioactivity determined by LSC.

The acetone extracts (<u>from the original sediment phase</u>) and water/ acetone sample (<u>from the original water phase</u>) were combined and treated as one sample. After acetone removal, the remaining aqueous phase was partitioned 3x with ethyl acetate. The organic extractable fraction was designated OR (organic fraction). The material left in the aqueous phase was designated polar nonextractable (PNE).

analysis

LSC -- extracts, material released from soil by combustion
HPLC -- gradient with acetonitrile vs KH_2PO_4 /K_2HPO_4 /MeOH /tetrabutyammoniumbromide(TBAB)
GC/MS -- methylated derivatives
LC/MS

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

RESULTS

Based on the percent distribution found in the organic extractable fractions, the amount of SDS-67042 increased rapidly within the first 24 hours and reached its highest level for the salt water system at 29.16% of the applied ^{14}C-Chlorothalonil equivalent at 9 days and for fresh water reached 30.87% at 24 hours.

Amounts of SDS-67042 sulfoxide found in salt water and fresh water also increased through the first 9 days to peak concentrations of 12.08% and 16.53% respectively. After the levels of SDS-67042 and its sulfoxide reached their highest levels they continued to be metabolized further through the remaining 20 days to a mixture of polar non-extractables, but not [sic] new significant individual metabolic products were observed.

CONCLUSIONS

These results demonstrate that Chlorothalonil is rapidly metabolized in aqueous sediment systems using both salt water and fresh water sediments. These conversions appear to be of microbial origin involving attack on Chlorothalonil by glutathione (or other sulfur species) and probably occur at the water/sediment interface. The predominant metabolic pathways appear to involve initial attack by sulfur species which undergo further conversion to produce the benzisothiazol-3-one and its sulfoxide. Further metabolism results in decline of the levels of these two major metabolites with bound residues and polar water soluble materials resulting.

VII. Reviewer's Comments:

1) The reaction is clearly not pseudo-first-order, since the semilog plot of time vs concentration is far from linear. One might speculate that other mechanisms might be operating, such as initial binding to and subsequent release from soil [organic matter?]. It seems certain that aerobic aquatic metabolism occurs readily, although an initial half-life of 1 - 2 hours may be a somewhat too optimistic depiction of actual "pure" metabolic behavior.

1) Binding occurred almost instantly. Unbound parent decreased rapidly (down from ca. 40% to ca. 20% after 1 hr), and represented slightly more than 1% of the applied by day 30. No degradate showed a tendency to persist. The major degradate, SDS 67042 (the "thiazole" derivative), had its highest observed value of 29% at the 9th day and decreased to roughly half the 9 day value when sampling was discontinued at day 30. The other major derivative, SDS 67042 sulfoxide, rose to a peak of ca. 12% by day 9, and decreased to ca. 9% by day 30. The "post-extraction solid" material, representing bound substances, appeared to increase briefly, and then remain steady at ca. 30 - 35% of applied.

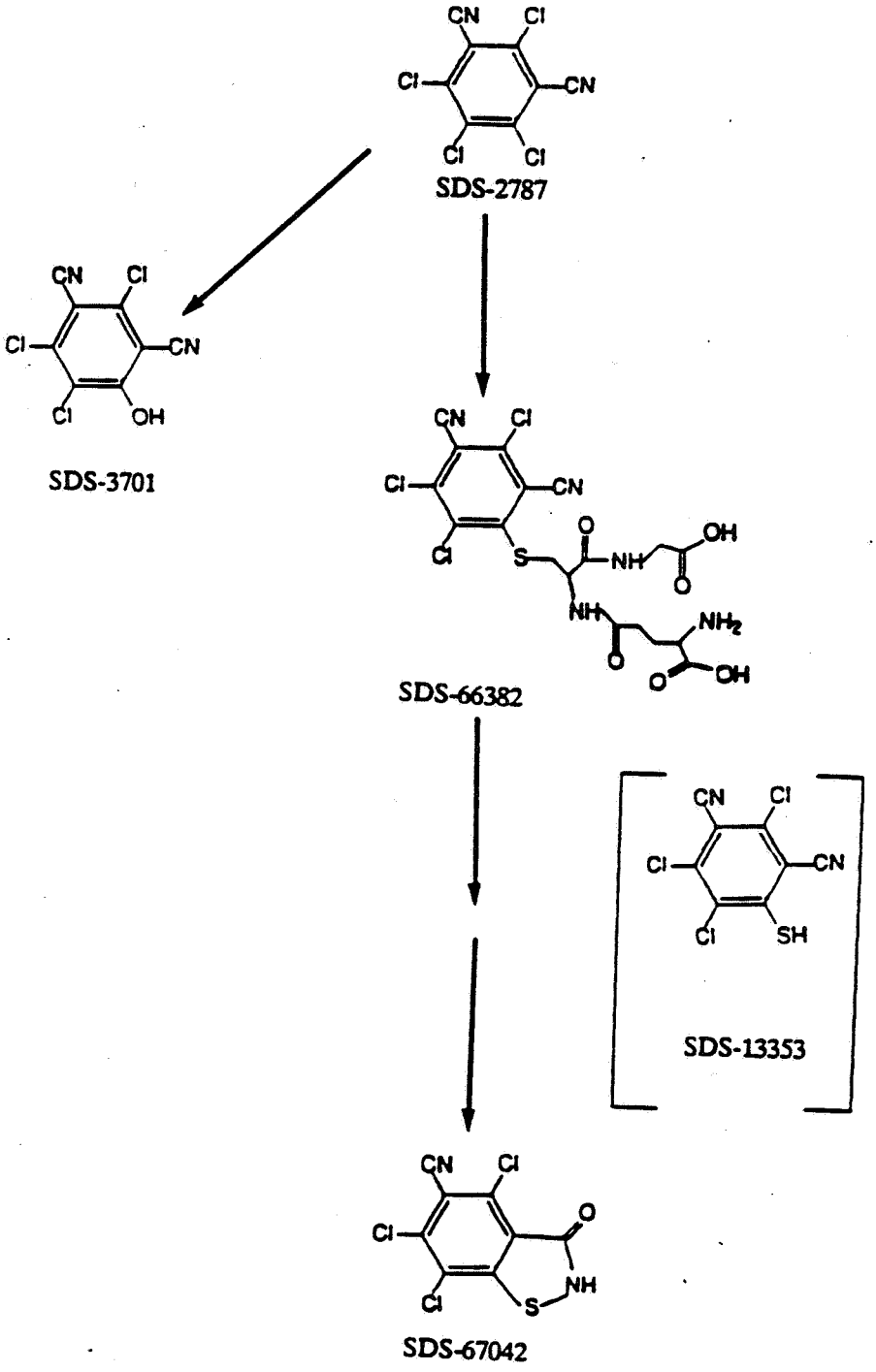
2) The overall recovery appears to have been satisfactory.

3) The radiopurity of the test compound is not stated.

VIII. CBI Information Addendum: attached

bcp

Figure 37. Metabolic Pathway of Chlorothalonil in Sediment/Water Systems



DATA EVALUATION REVIEW 2

I. Study Type: residues on turf clippings, EEB Guideline number 171-4

II. Citation:

King, C., Ballee, D.L., and Marks, A.F. Residues of Tetrachloro-isophthalonitrile (Chlorothalonil, SDS-2787) on Turf Clippings - 1985. performed by Ricerca, Inc. Painesville, OH, sponsored by Fermenta Plant Protection Company, Painesville, OH. received 2/27/92 under MRID# 422220-01.

King, C., and Ballee, D.L. Residues of 4-Hydroxy-2,5,6-trichloro-isophthalonitrile (Chlorothalonil, SDS-2787) on Turf Clippings - 1985. performed by Ricerca, Inc. Painesville, OH, sponsored by Fermenta Plant Protection Company, Painesville, OH. received 2/27/92 under MRID# 422220-02.

Cassidy, P.S., Dillon, K.A., and Ballee, D.L. Residues of Tetrachloro-isophthalonitrile (Chlorothalonil, SDS-2787), SDS-3701, SDS-46851, HCB, and PCBN on Turf Clippings - 1985. performed by Ricerca, Inc. Painesville, OH, sponsored by Fermenta Plant Protection Company, Painesville, OH. received 2/27/92 under MRID# 422220-03.

III. Reviewer

Typed Name:	E. Brinson Conerly-Perks	E.B. Conerly-Perks
Title:	Chemist, Review Section 3	12/15/92
Organization:	EFGWB/EFED/OPP	

IV. Conclusions:

None of the studies was submitted as an EFGWB turf field dissipation study, and none is acceptable as such, due to the impossibility of confirming the application rate and to the lack of data on residues in compartments other than the top parts of the grass. Because they are all clearly unacceptable to fulfill EFGWB guidelines, the studies will not be discussed in detail in this review, but only summarized.

The submitted data are intended to show that, using practices common to golf course greens, Chlorothalonil residues do not accumulate on the grass. The data do appear to be consistent with lack of accumulation in the grass, since concentrations in the clippings do decrease. These observations are likely to result from the physical removal of the portion of grass that the treatment has reached (by mowing, and subsequently taking away the clippings) and not from any actual chemical transformation. It should be noted that the regimen under which the grass was maintained is very specific for golf greens, i.e. daily mowing, etc., and would not be similar to that of home lawns or unmaintained grassland. The rapid disappearance from the grass which was observed here may not occur elsewhere. The registrant makes the implicit assumption that the top part of the grass intercepts all or most of the chemical and therefore represents the exposure risk to humans and/or wildlife. However, exposure could occur through some means other than the grass, and the

submitted material does not provide any means of assessing these possibilities. There is no specific information in the study as to residues in any medium other than grass, e.g. soil or water. If mowing and clipping removal are carefully done, this might be effective in mitigating exposure from grass.

Incidentally, the 1991 study appears to encompass information similar to that in the earlier two, and also include data on several other analytes as well.

V. Materials and Methods

ABSTRACT -- MRID# 422220-01

In this study, turf clippings were analyzed for chlorothalonil on two sets of samples; one set was collected from the 19th practice green at Deer Lake Golf Course, Geneva, Ohio and another set of samples was collected from the 19th practice green from Quail Hollow Golf Course, Painesville, Ohio. Each collection contained samples before DACONIL 2787 Flowable Fungicide application and continuous sampling with each mowing after treatment.

Statistical evaluation on the data generated by this study indicates that the residue level of chlorothalonil declines, exponentially at the rate of 46.6 percent per day with normal mowing. This estimate by using a logarithmic scale, for example the decline from one day to the next, converts to a percent difference on the original (ppm) scale. Observations, equations and tables used by the statistician are detailed in APPENDIX II.

ABSTRACT -- MRID# 422220-02

In this study, turf clippings were analyzed for SDS-3701 on two sets of samples; one set was collected from the 19th practice green at Deer Lake Golf Course, Geneva, Ohio and another set of samples was collected from the 19th practice green from Quail Hollow Golf Course, Painesville, Ohio. Samples were taken before application of DACONIL 2787 Flowable Fungicide, and again with each mowing after treatment. The levels of SDS-3701 residues on Quail Hollow samples were significantly higher than the levels on Deer Lake samples. However, two applications of DACONIL 2787 Flowable Fungicide ... had been made at the Quail Hollow Golf Course prior to the conduct of the study, while no previous applications of DACONIL 2787 Flowable Fungicide had been made to Deer Lake Golf Course in 1985. At both golf courses loss of SDS-3701 on grass clippings was observed over a period of time.

ABSTRACT -- MRID# 422220-03

In this study, turf clippings from four greens located at Quail Hollow Golf Course, Painesville, Ohio, were analyzed for residues of Chlorothalonil (SDS-2787), SDS-3701, SDS-46851, HCB and PCBN. The samples were taken before application of Daconil 2787 Flowable Fungicide, and again with each day's mowing after treatment (days one to seven). A total of 3 treatments were applied to the 4 greens. As this golf course uses Chlorothalonil for turf maintenance of its greens, previous applications of Daconil 2787 Flowable Fungicide had been made at the test sites thus accounting for the presence of all the compounds in pretreated grass clippings. After treatment, declines were seen in the residues of Chlorothalonil (SDS-2787), HCB and PCBN. A statistical calculation of the data indicates that the decline rate in residue level is 46% per day for SDS-2787, 35% for HCB, and 45% for PCBN. The predicted cumulative declines within 7 days were 99% for Chlorothalonil and PCBN and 95% for HCB. Residues of SDS-3701 and SDS-46851 were fairly constant throughout the study except for days one to three after each application when SDS-3701 showed a noticeable decline. The data demonstrate that the metabolites will not build up in turf with repeated applications of Daconil 2787 Flowable Fungicide.

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

MRID# 422220-01:

In this study, turf clippings were analyzed for Chlorothalonil on two sets of samples; one set was collected from the 19th practice green at Deer Lake Golf Course, Geneva, Ohio and another set of samples was collected from the 19th practice green from Quail Hollow Golf Course, Painesville, Ohio. Each collection contained samples before DACONIL 2787 Flowable Fungicide application and continuous sampling with each mowing after treatment.

Statistical evaluation on the data generated from this study indicated that the residue level of Chlorothalonil declined exponentially at the rate of 46.6 percent per day with normal mowing. This estimate was made by using a logarithmic transformation of the data where a difference on the logarithmic scale, for example the decline from one day to the next, converted to a percent difference on the original (ppm) scale. Observations, equations and tables used by the statistician are detailed in Appendix II.

The results of the study indicate a rapid decline over time in the amount of Chlorothalonil residue found in turf clippings from golf greens treated with DACONIL 2787 Flowable Fungicide. Analysis of the study data provided an estimate of the rate of decline in Chlorothalonil residues of 46.6% per day, with a 95% confidence range of 44 to 49%.

MRID# 422220-02:

In this study, turf clippings were analyzed for SDS-3701 on two sets of samples; one set was collected from the 19th practice green at Deer Lake Golf Course, Geneva, Ohio and another set of samples was collected from the 19th practice green from Quail Hollow Golf Course, Painesville, Ohio. Each collection contained samples before DACONIL 2787 Flowable Fungicide application and continuous sampling with each mowing after treatment.

A maximum mean level of 0.77 ppm SDS-3701 was detected on Deer Lake samples taken 1 day following a field application. Deer Lake samples taken at intervals longer than 1 day following an application contained less than 0.50 ppm SDS-3701 (the non-detect level). A maximum mean level of 6.69 ppm SDS-3701 was detected on Quail Hollow samples. The levels of SDS-3701 residues on Quail Hollow samples were significantly higher than the levels on Deer Lake samples and remained at the same level longer before starting to decline. This probably is due to a combination of higher rate of DACONIL 2787 Flowable Fungicide applied in this study and to the use of DACONIL 2787 Flowable Fungicide in the normal greens maintenance program earlier in the season at Quail Hollow. The earlier applications of fungicide probably also account for the detection of SDS-3701 in the "pre-spray" samples from Quail Hollow. There were no previous sprays of DACONIL 2787 Flowable Fungicide prior to the conduct of this study at Deer Lake Golf Course. At both golf courses loss of SDS-3701 on grass clippings was observed over a period of time with subsequent mowings.

MRID# 42220-03:

Green clippings from four greens at Quail Hollow Golf Course, Painesville, Ohio, were analyzed for residues of Chlorothalonil, HCB, PCBN, SDS-3701, AND SDS-46851. The samples were taken before application of DACONIL 2787 Flowable Fungicide, and again with each day's mowing after treatment for seven days. A total of 3 treatments were made to the four greens. Previous applications had been made at the test sight [sic] account for the presence of all the compounds in pretreated grass clippings. After treatment declines of Chlorothalonil, HCB, and PCBN were found. Residues of SDS-3701 and SDS-46851 were fairly stable except for a decline of SDS-3701 between days 1 and 3 after each application.

The information from the study is important in estimating half-lives and rates of decline for Chlorothalonil, HCB and PCBN on turf. It also demonstrates the level of SDS-3701 and SDS-46851 that can be expected following successive application of DACONIL 2787 to turf and that there is no build up of these metabolites.

VII. Reviewer's Comments:

1) These studies do not definitively demonstrate the hypothesis they have been submitted to support, i.e. that mowing and removal of clippings decrease to negligible levels the exposure of wildlife to Chlorothalonil. Due to a number of factors, the data cannot be interpreted with confidence. Major reasons are discussed below.

2) The information provided is consistent with, but does not prove, rapid disappearance and lack of persistence and/or build-up.

3) The processes which are occurring in the reported studies cannot be discerned. There might be migration or degradation or a mixture of both. In fact, in view of the way the study was performed, the findings might be due simply to the gradual physical removal of the part of the grass which had intercepted the pesticide, without the necessity for any other process.

bcp

4) Moreover, in all three studies, the amounts recovered cannot be related to the total amount applied -- e.g., what percentage did the turf intercept? A direct comparison of the concentration found in the turf and the amount applied is meaningless, since the total weight of grass clippings in each case is not known (or knowable).

In a field dissipation study submitted to EFGWB, there would normally be information not only on the crop residues, but soil residues as well. EFGWB recognizes that these studies are not, and were not submitted as, field dissipation studies.

5) Despite several readings of MRID# 422220-03, this reviewer is unable to find the application rate used in this study. In the other studies, application rate cannot be confirmed from the information given.

VIII. CBI Information Addendum: n.a.

bcp

Environmental Fate & Effects Division
PESTICIDE ENVIRONMENTAL FATE ONE LINE SUMMARY
CHLOROTHALONIL
Last Update on December 15, 1992
[V] = Validated Study [S] = Supplemental Study [U] = USDA Data

LOGOUT	Reviewer: EBQP	Section Head:	Date:

Common Name:CHLOROTHALONIL
Smiles Code:Cl-c(c(Cl)c(c1Cl)C#N)c(Cl)c1C#N
PC Code # : 81901 CAS #:1897-45-6 Caswell #:

Chem. Name :TETRACHLOROISOPHTHALONITRILE

Action Type:Fungicide

Trade Names: BRAVO; CLORTOCAFFARO; CLORTOSIP; DACONIL 2787
(Formul'tn):WP;G; PELLET; L; SOLUBLE CONC.
Physical State: COLORLESS ODORLESS CRYST.

Use :FRUITS/VEGETABLES/PEANUTS/TURF/ORNAMENTALS
Patterns :
(% Usage) :
:

Empirical Form: $C_8Cl_4N_2$
Molecular Wgt.: 265.91 Vapor Pressure: 2.00E -6 Torr
Melting Point : 250 °C Boiling Point: 350 °C
Log Kow : 2.88 pKa: @ °C
Henry's : 5.83E -7 Atm. M3/Mol (Measured) 5.83E -7 (calc'd)

Solubility in ...					Comments
Water	1.20E	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
[V] pH 7.0: STABLE
[V] pH 9.0:10% DEGRADED IN 30 DAYS
[ ] pH :
[ ] pH :
[ ] pH :

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Photolysis (161-2, -3, -4)
[ ] Water:STABLE
[ ] :
[ ] :
[ ] :

[ ] Soil :STABLE
[ ] Air :

Aerobic Soil Metabolism (162-1)

	SOIL	NONSTERILE	STERILE
[S]	SiLm	36.5 DAYS	213.8 DAY
[S]	LOAM	14.7 "	31.3 "
[S]	SdLm	12.8 "	18.0 "
[S]	SdLm	10.3 "	21.9 "

[ ]
[ ]

Anaerobic Soil Metabolism (162-2)
[ ]
[ ]
[ ]
[ ]
[ ]
[ ]
[ ]

Anaerobic Aquatic Metabolism (162-3)
[V] SiLm 9 DAYS
[V] SdLm 10 DAYS (LOG PLOT IS NON-LINEAR FOR BOTH)
[ ]
[ ]
[ ]
[ ]
[ ]

Aerobic Aquatic Metabolism (162-4)
[V] SiLm - fresh 1.4 hr, salt, 1.04 hr
[ ]
[ ]
[ ]
[ ]
[ ]
[ ]

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Soil Partition Coefficient (Kd) (163-1)
[ ] 20 SANDY LM 3.5%OM
[ ] 3 SAND 0.6%OM
[ ] 29 SILT 0.8%OM
[ ] 26 SILTY CL LM 3.2%OM
[ ]
[ ]

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

Laboratory Volatility (163-2)
[ ]
[ ]

Field Volatility (163-3)
[ ]
[ ]

Terrestrial Field Dissipation (164-1)
[ ] 26-56 DA (SOIL?)
[ ]
[ ]
[ ]
[ ]
[ ]
[ ]
[ ]
[ ]
[ ]

Aquatic Dissipation (164-2)
[ ]
[ ]
[ ]
[ ]
[ ]
[ ]

Forestry Dissipation (164-3)
[ ]
[ ]

Long-Term Soil Dissipation (164-5)
[ ]
[ ]

Accumulation in Rotational Crops, Confined (165-1)
[V] RESIDUES DETECTED
[ ]

Accumulation in Rotational Crops, Field (165-2)
[V] RESIDUES DETECTED, TOLERANCE SETTING REQUIRED
[ ]

Accumulation in Irrigated Crops (165-3)
[ ]
[ ]

Bioaccumulation in Fish (165-4)
[ ] BLUEGILL 75X EDIBLE; 514X VISCERA; 264 WHOLE (1984 REG STD)
[ ] CATFISH 9.4X EDIBLE;25X VISCERA; 16X WHOLE

Bioaccumulation in Non-Target Organisms (165-5)
[ ]
[ ]

Ground Water Monitoring, Prospective (166-1)
[ ] Protocol has been submitted and reviewed. Most likely a study
[ ] will conducted in North Carolina on peanuts.
[ ]
[ ]

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

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

Ground Water Monitoring, Miscellaneous Data (158.75)
[V] DETECTED IN ONLY TWO LOCATIONS - - LONG ISLAND AND CAPE COD
[ ]
[ ]

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Field Runoff (167-1)
[ ]
[ ]
[ ]
[ ]

Surface Water Monitoring (167-2)
[ ]
[ ]
[ ]
[ ]

Spray Drift, Droplet Spectrum (201-1)
[ ]
[ ]
[ ]
[ ]

Spray Drift, Field Evaluation (202-1)
[ ]
[ ]
[ ]
[ ]

Degradation Products

4-hydroxy-2,5,6-trichloro-isophthalonitrile
2,4,5,6-tetrachloroisophthalimide (only degradate in hydrolysis)
3-cyano-2,4,5,6-tetrachlorobenzamide
2-hydroxy-5-cyano-3,4,6-trichlorobenzamide
3-carboxy-2,5,6-trichlorobenzamide

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Comments

Koc = 1380 (U)

References: Wauchope et al. 1992 Reviews of Env. Contam Tox.
Writer : PJH, JKW 123:1-164