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To: Joanne Miller
 Product Manager PM 23
 Registration Division (H7505C)

From: Akiva D. Abramovitch, Ph.D., Head
 Environmental Chemistry Review Section #3
 Environmental Fate & Ground Water Branch/EFED (H7507C)

Thru: Henry Jacoby, Chief
 Environmental Fate & Ground Water Branch/EFED (H7507C)

Attached, please find the EFGWB review of...

Reg./File #: 055947-UR

Chemical Name: N³,N³-Di-n-propyl-2,4-dinitro-6-(trifluoromethyl)-m-phenylenediamine

Type Product: herbicide

Product Name: n.a.

Company Name: Sandoz Crop Protection Corporation

Purpose: submission of additional fish bioaccumulation data

Action Code: 116 EFGWB #(s): 92- 0214 Total Review Time: _____ days

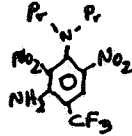
EFGWB Guideline/MRID Summary Table: The review in this package contains...				
161-1	162-1	164-1	165-1	166-1
161-2	162-2	164-2	165-2	166-2
161-3	162-3	164-3	165-3	166-3
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201-1	163-1	164-5	165-5	167-2
202-1	163-3			



Prodiamine 92-0214

1. CHEMICAL:

chemical name: N³,N³-Di-n-propyl-2,4-dinitro-6-(trifluoromethyl)-m-phenylenediamine
common name: Prodiamine
trade name: Endurance
structure:
CAS #: 29091-21-2
Shaughnessy #: 110201



PHYSICAL/CHEMICAL CHARACTERISTICS are as follows:

physical state -- crystalline powder
color -- dark yellow
odor -- odorless
M.P. -- 124-125° C
vapor pressure -- 2.5×10^{-7} mm Hg at 25° C
water solubility -- 0.05 ppm
octanol/water coefficient (k_{ow}) -- 3.3×10^4

2. TEST MATERIAL: described in DER

3. STUDY/ACTION TYPE: submission of additional fish bioaccumulation data

4. STUDY IDENTIFICATION:

appendix 1 to Forbis, A. and Georgie, L., D. Uptake and Bioconcentration of ¹⁴C-Prodiamine by Bluegill (*Lepomis Macrochirus*). performed by Analytical Bio-Chemistry Laboratories, Inc., Columbia, MO. Submitted by Sandoz Crop Protection Corporation, Chicago, IL. dated 10/11/85. received 2/23/88 under MRID# 405238-01

5. REVIEWED BY:

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

E.B. Conerly-Perks 12/19/91

6. APPROVED BY:

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

Akiva Abramovitch
DEC 19 1991

7. CONCLUSIONS:

- 1) The appendix to MRID# 405238-01, discussed in this review, provides the necessary information on residue characterization. The previously accepted bioaccumulation factors were determined in the study described in MRID# 417272-01. Taken together, these two reports are marginally acceptable to fulfill the requirement for fish bioaccumulation data. It should be noted that the applicant is combining information from these two separate and distinct studies to fulfill the data requirement.
- 2) MRID# 417272-01 indicates significant uptake of Prodiamine, resulting in BCF values of 390, 1200, and 2000X for the fillet, whole fish, and viscera, respectively. Depuration was essentially complete (>90%) in 14 days. MRID# 405238-01 provides the following additional information:

- 1) The majority of residue in the 21 and 28 day tissues (fillet and viscera) is present as parent (ca. 55% on average) and des-propyl prodiamine (ca. 7% on average).
- 2) There are a number of other metabolites present which were not identified due to their small quantities.

8. RECOMMENDATIONS:

The applicant should be informed that no further data on fish bioaccumulation are required at this time.

9. BACKGROUND:

Prodiamine is an not-yet-registered herbicide used to control the germination of grasses and broadleaf weeds in ornamentals and turf. Label directions indicate that it may be applied either to a cover crop (established turf) or to bare soil (around ornamental plants and in non-crop areas). The recommended label rate is up to 1.15 lb ai./A (1.15 ppm, 3" soil layer) per single application or 2.3 lb a.i./A/yr.

GROUND WATER ASSESSMENT

Available data indicate that Prodiamine is stable to hydrolysis, but (based on a 1980 review) is highly susceptible to photolysis in aqueous solution. It metabolizes slowly under aerobic conditions and (based on a 1980 review) is not mobile in laboratory studies. A recent field study on turf also seems to indicate that Prodiamine is not mobile. Because of its extremely short photolytic half life and lack of mobility, Prodiamine does not appear likely to reach ground water. Though it is improbable that it would reach ground water, if somehow it did, it would persist there, since photolysis, the major mode of degradation, would not occur. The mobility of the major degradate (Prodiamine benzimidazole) has still not been defined by acceptable data, and it appears to be persistent. The likelihood of Prodiamine benzimidazole to reach ground water, and its fate under such conditions, is not known.

SURFACE WATER ASSESSMENT

Prodiamine does not appear to be a major threat to sunlight-exposed surface water since it photolyzes rapidly in water. Although the probability seems very low, any Prodiamine which is present on soil affected by a runoff event could be carried on suspended particles to adjacent bodies of surface water. Once there, it would be expected to remain in the sediment and degrade/dissipate very slowly.

ENVIRONMENTAL FATE DATA BASE ASSESSMENT

The status of data requirements is as follows:

hydrolysis -- FULFILLED 6/22/90 [Bowman and Fenessey, MRID #'s 406091-01 and 413594-01 -- $t_{1/2}$ > 6 months is indicated at all three pHs

photolysis in water -- FULFILLED 5/13/80 [reference not indicated in that review] -- not done under current Guidelines. A short half life (ca. 20 min.) is indicated. The fulfilling study has not been rereviewed under current standards.

soil photodegradation -- a study has recently been submitted and will be reviewed in due course. A previously submitted study [reference not indicated in that review] unacceptable as of 5/13/80, not required for this use

aerobic soil metabolism -- FULFILLED 6/22/90 [Krueger and Butz, MRID #s 405934-24 and 413594-02]-- half-life ca. 2 mos, one major product

anaerobic soil metabolism -- submitted study unacceptable as of 5/14/80, not required for this use

leaching/adsorption/desorption -- FULFILLED 5/13/80 for parent [reference not indicated in that review. A batch adsorption/desorption study (MRID 405934-25, which was probably not the fulfilling study) indicated K_d values of 19.5 to 399 for adsorption. NEW STUDY REQUIRED ON AGED MATERIAL [as of 6/22/90 -- Daly, MRID #s 405934-26 and 413594-03 are not acceptable]. The mobility of primary degradate (Prodiamine benzimidazole) has not been satisfactorily defined at this time, although it is apparently also relatively immobile.

turf terrestrial field dissipation -- FULFILLED 6/22/90 [Bade and Rosas, MRID# 413594-05] -- no leaching or significant dissipation noted.

confined accumulation on rotational crops -- FULFILLED 5/14/80 [reference not indicated in that review] -- not done under current Guidelines - - not required for this use -- no significant accumulation except in root crops

fish bioaccumulation -- FULFILLED by MRID# 417272-01 (reviewed 7/25/91), and additional data in MRID 405238-01 which is discussed in this review

10. DISCUSSION OF INDIVIDUAL TESTS OR STUDIES: see DER
11. COMPLETION OF ONE-LINER: updated 1-liner attached
12. GBI APPENDIX: attached to DER

DATA EVALUATION REVIEW 1

I. Study Type: fish bioaccumulation, Guideline 165-4

II. Citation:

appendix 1 to Forbis, A. and Georgie, L., D. Uptake and Bioconcentration of ¹⁴C-Prodiamine by Bluegill (*Lepomis Macrochirus*). performed by Analytical Bio-Chemistry Laboratories, Inc., Columbia, MO. Submitted by Sandoz Crop Protection Corporation, Chicago, IL. dated 10/11/85. received 2/23/88 under MRID# 405238-01

III. Reviewer:

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

E. B. Conerly-Perks

IV. Conclusions:

The appendix provides the necessary additional information which marginally fulfills the requirement for metabolite identification. No further data are required at this time. MRID# 417272-01, a separate and distinct study, indicates significant uptake of Prodiamine, resulting in BCF values of 390, 1200, and 2000X for the fillet, whole fish, and viscera, respectively. Depuration was essentially complete (>90%) in 14 days. The appendix in MRID# 405238-01 provides the following additional information on residue characterization:

- 1) The majority of residue in the 21 and 28 day tissues (fillet and viscera) is present as parent (ca. 55% on average) and des-propyl prodiamine (ca. 7% on average)
- 2) There are a number of other metabolites present which were not identified due to the small quantities present.

V. Materials and Methods:

analytical methods

thin layer chromatography -- used to separate prodiamine and its metabolites

radioassay -- used to analyze aqueous and organic solutions and ¹⁴CO₂ from combustion of solid samples

gas chromatography -- analysis of parent and metabolites

mass spectrometry -- confirmation of prodiamine and N-des-propylprodiamine

extraction -- 5 gm fillet, viscera, or whole fish were homogenized with 30 ml of acetone/methanol (1:1) and then filtered. The solid was re-extracted 2 more times with fresh acetone/methanol solution. Solvent was removed under reduced pressure, and the residue taken up in 20 ml H₂O. This solution was partitioned 3x with 40 ml of ethyl acetate. The three extracts were combined and radioassayed. The remaining solution was dried with anhydrous sodium sulfate, filtered, and then all ethyl acetate removed. The oily residue was partitioned between acetonitrile and hexane. The acetonitrile layer was reduced to a small volume for TLC analysis. The aqueous layer after ethyl acetate extraction was combined with the solid, adjusted to 1N HCl

bcp

Prodiamine 92-0214

-5-

and then refluxed for 1 hour. The mixture was extracted 3x each with 40 ml of ethyl acetate. The combined ethyl acetate extracts (designated acid-released metabolites) was radioassayed, dried over sodium sulfate and reduced to small volume for TLC analysis. The remaining aqueous layer and solid were also radioassayed.

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

RESULTS

Metabolite Characteristics:

Radiocarbon characteristics in fillet and viscera from fish exposed to ^{14}C -Prodiamine for 21 days and 28 days are presented in table 2. Between 65 to 87% of radiocarbon in fish could be readily extracted and partitioned into ethyl acetate layer (designated as free metabolites). Fillet generally had higher percentage of free metabolites (84% in 21-day sample and 87% in 28-day sample) when compared with viscera (65% in 21-day sample and 69% in 28-day sample).

The free metabolites fraction contained oily substances which could be readily cleaned-up by partitioning between acetonitrile and hexane layers. Most of the ^{14}C (over 80%) partitioned to the acetonitrile layer while most of the oily substances stayed in the hexane layer. The acetonitrile fraction could be easily analyzed by TLC.

The acid-released metabolites accounted for 3 to 17% of total tissue ^{14}C , with the visceral samples containing a higher percentage of releasable radiocarbon when compared to the fillet samples. The acid-released metabolites were ready for TLC analysis without further clean-up.

The water-soluble radiocarbon accounted for 3 to 14% of total tissue ^{14}C , with the visceral samples containing a higher percentage of radiocarbon, when compared to the fillet samples. Between 6 to 14% of the tissue radiocarbon remained in the solid and could not be extracted.

Metabolite Identification:

The free and acid-released metabolites were separated by TLC into 8 ^{14}C bands. The metabolite distribution patterns of these two fractions were similar. The metabolite identification of the combined fractions are shown in table 3.

Band 1 accounted for about 65% of fillet radiocarbon and about 45% of viscera radiocarbon. Band 1 was identified as unchanged prodiamine by TLC co-chromatography with an authentic prodiamine in 3 solvent systems (table 1), by GC analysis, and by GC-MS.

Similarly, band 2 was identified as N-des-propyl prodiamine [2,4-dinitro- N^3 -propyl-6-(trifluoromethyl)-1,3-benzenediamine]. This compound accounted for ca. 8% of fillet ^{14}C and 4% of viscera ^{14}C .

Band 3 represented 2 to 7% of the radiocarbon in the sample. In solvent A, it had an r_f similar to that of an authentic reduced A metabolite (Table 1), but had different values in the other two solvents. It is designated as unknown I.

Bands 4 to 7 each individually represented 1 to 5% of tissue radiocarbon, and did not match any of 5 model metabolites by TLC analysis. They are designated unknown II to V.

The TLC origin material [in solvent A] accounted for about 12% of tissue radiocarbon. Since some of it could be moved above the origin in solvents B and C, it was not homogeneous. The identity of these materials was not determined due to the small amount of residue they represent.

CONCLUSIONS

Prodiamine was gradually metabolized in fish to N-despropyl prodiamine and other more polar metabolites and then eliminated from fish. Unchanged prodiamine accounted for about 55% of total fish residue while N-despropyl prodiamine accounted for about 7%. The remaining radiocarbon [residues] were polar, water soluble or unextractable.

VII. Reviewer's Comments:

Although there is a considerable amount of recovered material which has been isolated but not identified, it appears that the overwhelming majority of radiocarbon is parent. Unless there are further concerns about metabolites put forward by TOX branch, no further efforts at identification are required at this time.

VIII. CBI Information Addendum: attached

110201

PRODIAMINE

RIN 1786-93

Page ___ is not included in this copy.

Pages 8 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.

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

Last Update on December 18, 1991

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

LOGOUT	Reviewer:	Section Head:	Date:
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Common Name: PRODIAMINE

PC Code # : 110201

CAS #: 29091-21-2

Caswell #:

Chem. Name : N3,N3-Di-n-propyl-2,4-dinitro-6-(trifluoromethyl)-m-phenylene diamine

Action Type: HERBICIDE

Trade Names: Endurance

(Formul'tn):

Physical State:

Use : TO CONTROL THE GERMINATION OF GRASSES AND BROADLEAF WEEDS
 Patterns : IN ORNAMENTALS AND TURF
 (% Usage) :

Empirical Form: $C_{13}H_{17}N_4O_4F_3$
 Molecular Wgt.: 350.30 Vapor Pressure: 2.50E -7 Torr
 Melting Point : °C Boiling Point: °C
 Log Kow : 3.3E4 pKa: e °C
 Henry's : E Atm. M3/Mol (Measured)

Solubility in ...

Water	E	ppm	@	°C	Comments
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	

Hydrolysis (161-1)

[V] pH 5.0: STABLE
 [V] pH 7.0: STABLE
 [V] pH 9.0: STABLE
 [] pH :
 [] pH :
 [] pH :

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

[V] Water: ABOUT 20 MINUTES

[] :
[] :
[] :

[] Soil :
[] Air :

Aerobic Soil Metabolism (162-1)

[S] ABOUT 2 MONTHS

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Anaerobic Soil Metabolism (162-2)

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Anaerobic Aquatic Metabolism (162-3)

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Aerobic Aquatic Metabolism (162-4)

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Environmental Fate & Effects Division
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PRODIAMINE

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Soil Partition Coefficient (Kd) (163-1)

[]	SOIL	Kads	Koc
[V]	SAND	19.54	19,540
[V]	SILT LOAM	54.47	10,890
[V]	CLAY LOAM	181.6	9,310
[V]	SANDY LOAM	398.5	12,860
[]	(UNAGED STUDY)		

Soil Rf Factors (163-1)

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[]
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Laboratory Volatility (163-2)

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[]

Field Volatility (163-3)

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Terrestrial Field Dissipation (164-1)

[V] PARENT AND MAJOR DEGRADATE DO NOT LEACH
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Aquatic Dissipation (164-2)

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Forestry Dissipation (164-3)

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PRODIAMINE

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Long-Term Soil Dissipation (164-5)

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[]

Accumulation in Rotational Crops, Confined (165-1)

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Accumulation in Rotational Crops, Field (165-2)

[]
[]

Accumulation in Irrigated Crops (165-3)

[]
[]

Bioaccumulation in Fish (165-4)

[V] BCFs 390 (FILLET), 1200 (WHOLE), 2000 (VISCERA)
[] RESIDUE IS CA. 55% PARENT AND 5% DES-PROPYL PRODIAMINE

Bioaccumulation in Non-Target Organisms (165-5)

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[]

Ground Water Monitoring, Prospective (166-1)

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

[]
[]
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[]

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

[]
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Ground Water Monitoring, Miscellaneous Data (158.75)

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PRODIAMINE

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Field Runoff (167-1)

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Surface Water Monitoring (167-2)

[]
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[]

Spray Drift, Droplet Spectrum (201-1)

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[]

Spray Drift, Field Evaluation (202-1)

[]
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Degradation Products

6-amino-2-ethyl-7-nitro-1-propyl-5-trifluoromethyl-benzimid-azole
Des-Propyl Prodiamine (fish metabolism)

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Comments

In the study of confined accumulation on rotational crops, there was no accumulation except in root crops.

References:

Writer : PJH, EBC (12/18/91)