



JAA

Shaughnessy No.: 125301

Date Out of EFGWB: JUL - 2 1990

To: Mr. Phillip Hutton
Product Manager # 25
Registration Division (TS-767)

From: Paul Mastradone, Ph.D., Chief
Environmental Chemistry Review Section #1
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 #: 35977-EUP-RG

Chemical Name: Fenoxycarb

Type Product: Insecticide

Product Name: LOGIC

Company Name: Maag Agrochemicals

Purpose: Review of EUP proposal

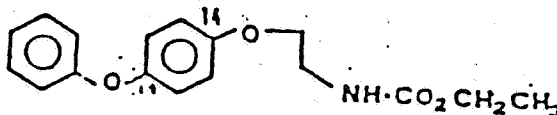
Action Code: 740 EFGWB #(s): 90777

Date Received: 12/15/88 Total Reviewing Time: 2 days

Deferrals to: ☐ Ecological Effects Branch
☐ Dietary Exposure Branch
☐ Non-Dietary Exposure Branch
☐ Toxicology Branch I
☐ Toxicology Branch II

1.0 CHEMICAL:

chemical name: Ethyl (2-[4-phenoxyphenoxy]-ethyl) carbamate
common name: Fenoxycarb
trade name: LOGIC Fire Ant Bait
structure:



CAS #:
Shaughnessy #:125301

2.0 TEST MATERIAL: discussed in DER

3.0 STUDY/ACTION TYPE:

Review of experimental use permit proposal to use fenoxycarb on abandoned pineapple fields in Hawaii.

4.0 STUDY IDENTIFICATION:

Nichols, R.L. 1989. Application for an EPA Non-Food Experimental Use Permit to Allow Testing of the Fenoxycarb Formulation LOGIC (fire) Ant Bait (EPA Reg. No. 35977-4) on Abandoned (Ratoon) Pineapple Fields in the State of Hawaii. sponsored and submitted by Maag Agrochemicals Vero Beach, Florida. Received by EPA on 9/6/89.

5.0 REVIEWED BY:

James A. Hetrick, Ph.D.
Chemist, ECRS # 1
EFGWB/EFED/OPP

Signature: *James A. Hetrick*
Date: 6/25/90

6.0 APPROVED BY:

Name: Paul Mastradone, Ph.D.
Section Chief, ECRS # 1
EFGWB/EFED/OPP

Signature: *Paul Mastradone*
Date: JUL -2 1990

7.0 CONCLUSIONS:

The EUP is based on the following terrestrial noncrop data requirements: hydrolysis, aerobic soil metabolism, adsorption/desorption, and fish accumulation. The following studies are scientifically sound and fulfill the Subdivision N data requirements: hydrolysis, aerobic soil metabolism, and fish accumulation. The soil column mobility studies provide supplemental data for the 163-1 data requirement. Therefore, the EUP is based on supplemental and acceptable data.

EFGWB is concerned that fenoxycarb dissipation cannot be predicted in Hawaiian soils for the following reasons: the laboratory

environmental fate studies were conducted with Swiss soils, and therefore, may not mimic the pesticide behavior in Hawaiian soils; and, the leaching and adsorption/desorption studies were conducted on finely-sieved Swiss soil which may underestimate fenoxycarb mobility. In addition, EFGWB is concerned that fenoxycarb is a non-target insecticide which may indiscriminately affect both terrestrial and aquatic arthropods other than big-headed ants. More important, fenoxycarb appears to bind to soil colloids, and therefore, may bind onto mobile surface-water sediments causing transport to aquatic environments. EFGWB concludes that if the EUP is granted, the studies should not be conducted on erodible soil that may enter bodies of water containing fish or aquatic invertebrates.

Based on the fate data, parent fenoxycarb appears to be moderately persistent ($t_{1/2} \approx 83$ days) in aerobic mineral soils. The predominate route of dissipation appears to be dependent on biological oxidation (i.e., CO_2 volatilization) with subsequent residue immobilization into nonlabile soil organic matter. Parent fenoxycarb appears to be immobile (K_d 18 to 70) in terrestrial ecosystem due to soil binding; however, additional data are necessary to adequately predict the mobility of fenoxycarb and its degradates in terrestrial ecosystems, especially in Hawaiian soils. Hence, the submitted fate data suggest that fenoxycarb is moderately persistent, and possibly immobile, in terrestrial ecosystems.

8.0 RECOMMENDATIONS: See Section 7.0

9.0 BACKGROUND:

Maag Agrochemicals Inc. is requesting an EUP to use fenoxycarb in abandoned pineapple fields for control of big-headed ants. The EUP proposal states that 1.75 lbs a.i., applied as a split broadcast application, will be used on 36 acres of abandoned pineapple fields. The experiment is expected to require 12 months to coordinate experiments at 3 different research sites.

10.0 DISCUSSION OF INDIVIDUAL TESTS OR STUDIES:

Please refer to attached DER'S for details concerning environmental fate studies. The following are summaries of the data required for the EUP:

Hydrolysis - The study (Dieterle and Kaufman, 00109328) is acceptable and fulfills the 161-1 data requirement.

Radiolabeled fenoxycarb did not hydrolyze in buffer solutions (pH 3, 7, and 9) incubated at 35 or 50°C. Parent fenoxycarb, therefore, does not hydrolyze under normal environmental conditions.

Aerobic Soil Degradation - The study (Dieterle, et. al. 00131804) is acceptable and fulfills the 162-1 data requirement.

Radiolabeled fenoxycarb in three Swiss soils had an average aerobic metabolism half-life of 83 days. During a 12 month incubation period, the ¹⁴C-fenoxycarb was respired as CO₂ (25% of applied ¹⁴C) or was found in intermediate phenolic metabolites (65% of applied ¹⁴C). The metabolites were tentatively identified as Ro-16-8797 (ethyl[2-(P-(P-ydroxyphenoxy) phenoxy)ethyl]carbamate) and Ro 17-3192. In addition unidentified polar compounds (accounting for less than 10% of the applied parent) were extracted from fenoxycarb treated soils. Hence, parent fenoxycarb degradation appears to be dependent on biological oxidation with subsequent residue incorporation into nonlabile soil organic matter.

Mobility-Leaching and Adsorption/Desorption - The mobility studies (Pyrde and Etterli, 001093323 and 00109333) do not satisfy the Subdivision N guidelines because the soils were finely sieved (< 0.5 to 0.8 mm particle-size distribution); finely-sieved soil increases the soil pesticide adsorption (based on soil mass) by concentrating clay and silt size particles. More important, the soil column leaching studies were conducted using only 40% of the required eluant volume. EFGWB believes the problems associated with these studies may consistently underestimate fenoxycarb mobility in terrestrial ecosystems.

The EUP is proposed to be conducted on Hawaiian soils; however, the laboratory studies were conducted on Swiss soils. EFGWB recognizes that soils of Swiss origin probably do not have similar chemical and physical properties as soils formed in Hawaii. Therefore, the mobility studies may not provide adequate data to assess fenoxycarb mobility in Hawaiian soil.

Based on supplemental data, radiolabeled fenoxycarb had a moderate to high adsorption affinity for soil colloids (K_d 18 to 77). In the soil column leaching studies, less than 1% of the applied ¹⁴C fenoxycarb was eluted through a moist-packed soil column. Parent fenoxycarb, therefore, appears to be immobile in terrestrial ecosystems due to soil binding.

Fish Accumulation - The study (Ellgehausen, 00148191) is acceptable and fulfills the 165-4 data requirement.

Radiolabeled fenoxycarb is bioaccumulated in whole fish, edible parts, and nonedible parts by 277.6X, 138.9X, and 439.6X, respectively. During a 14 day depuration period, the bioaccumulated ¹⁴C-fenoxycarb was eliminated from the fish tissue. The ¹⁴C-residues in fish tissue (edible and non-edible) were soluble in chloroform. The major degradate was identified as Ro 16-8797; otherwise, numerous unidentified polar degradates were detected by HPLC. Parent fenoxycarb does not appear to bioaccumulate in fish tissue.

11.0 COMPLETION OF ONE-LINER: N/A

12.0 CBI APPENDIX: There is no CBI used in this review.

DATA EVALUATION RECORD

STUDY IDENTIFICATION:

Dieterle, P. and R. Kaufman. 1982. Hydrolysis Study With the Radiolabeled Ro 13-5223/024. Report No. 041/2922. Maaq Agrochemicals. (MRID No. 00109328).

TYPE OF STUDY: Hydrolysis

REVIEWED BY:

James A. Hetrick, Ph.D., Chemist
Review Section 1, EFGWB/EFED

Signature: *James A. Hetrick*
Date: 3-2-90

APPROVED BY:

Paul J. Mastradone, Ph.D., Section Chief
Review Section 1, EFGWB/EFED

Signature: *Paul J. Mastradone*
Date: MAR - 2 1990

CONCLUSIONS:

EFGWB concludes that this study is scientifically valid and satisfies the data requirement for a hydrolysis study. The results of the study indicate that fenoxycarb is stable to hydrolysis in solutions buffered to pH 3, 7, and 9.

Based on the results of this study, EFGWB concludes that fenoxycarb will be stable to hydrolysis at pH levels found in the environment.

MATERIALS AND METHODS:

Radiolabeled ^{14}C -Fenoxycarb (specific activity 36.06 uCi/mg, radiochemical purity $\geq 98\%$, chemical purity (GC) $\geq 99\%$) was added to sterile buffered solutions (pH 3, 0.1 M phosphate; pH 7, 0.1 M phosphate) and pH 9, 0.2 borate) at 0.97 $\mu\text{g ml}^{-1}$ concentration. The vessels were maintained at 35°C and 50°C in the dark. Samples were extracted with ethyl acetate after 0, 3, 4, 7, and 10 weeks (35°C) and 0, 2, 3, 5, and 7 weeks (50°C). Radioactivity in the aqueous and ethyl acetate fractions were quantitated by liquid scintillation counting (LSC). The nature of the radioactivity in each sample was investigated by high performance liquid chromatography (HPLC).

REPORTED RESULTS:

The authors report that the material balance (radioactivity recovery) ranged from 101.0% to 105.8% of the initially applied radioactivity during the course of the study. Under all conditions, fenoxycarb accounted for 97% to 101% of the applied radioactivity and recovered after 70 days incubation. Less than 9% of the radioactivity present did not correspond to fenoxycarb. Unextractable (i.e., water

soluble) radioactivity accounted for 0.1% to 0.4% of the applied radioactivity. Similar results were obtained with fenoxycarb in distilled water only. (Table 1). Based on the results of the study the authors concluded that fenoxycarb was stable to hydrolysis under the conditions of the study.

DISCUSSION:

EFGWB recognizes that acidic hydrolysis was conducted at a pH of 3. EFGWB accepts this experimental protocol; however, future hydrolysis experiments need to be conducted in only slightly-acidic solutions (i.e., pH 5) to simulate hydrolysis in natural waters.

TABLE 1 Summary of the hydrolysis results with Rn 13-5273/024

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(Values are percentages of initially applied radioactivity)

Conditions	Rn 13-5273 1) 2)	in water phase 1) 3)	Radioactivity recovery 1)
pH 3.0 / 35 °C 4)	100 ± 4	0.1 ± 0.1	101.8 ± 3.3
pH 3.0 / 50 °C 5)	100 ± 3	0.3 ± 0.2	105.7 ± 1.7
pH 7.0 / 35 °C 4)	99 ± 4	0.2 ± 0.0	103.4 ± 2.6
pH 7.0 / 50 °C 5)	101 ± 3	0.2 ± 0.1	105.8 ± 3.0
pH 9.0 / 35 °C 6)	97 ± 4	0.4 ± 0.1	101.4 ± 4.5
pH 9.0 / 50 °C 5)	98 ± 4	0.4 ± 0.1	104.0 ± 4.8
distilled water/ 35 °C 7)	96 ± 4	0.2 ± 0.0	101.0 ± 4.1
distilled water/ 50 °C 5)	99 ± 6	0.2 ± 0.1	104.2 ± 5.2

1) Values are expressed as mean ± standard deviation (n=5) for the 5 time points analysed

2) Analysed by radio-HPLC of the ethyl acetate phase

3) Water soluble radioactivity not extracted into ethyl acetate

4) Samples were incubated for 0, 15, 27, 46 and 70 days

5) Samples were incubated for 0, 13, 24, 34 and 51 days

6) Samples were incubated for 0, 20, 27, 46 and 70 days

7) Samples were incubated for 0, 27, 39, 46 and 70 days

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DATA EVALUATION RECORD

STUDY IDENTIFICATION:

Dieterle, P., et al. 1983. Laboratory Aerobic Soil Metabolism Studies With ¹⁴C-Ro-13-5223/024 Report No. 141/3644. Maag Agrochemicals. (MRID No. 00131804).

TYPE OF STUDY: Aerobic Soil Metabolism

REVIEWED BY:

James Hetrick, Ph.D., Chemist
Review Section 1, EFGWB, EFED

Signature: *James G. Hetrick*
Date: 3-2-90

APPROVED BY:

Paul Mastradone, Ph.D., Section Chief
Review Section 1, EFGWB/EFED

Signature: *Paul J. Mastradone*
Date: MAR - 2 1990

CONCLUSIONS:

This study is scientifically sound and satisfies the data requirement for the aerobic soil metabolism study. Although the study was conducted with Swiss soils, EFGWB accepts it as satisfying the data requirement.

Based on the results of the study, EFGWB concludes that fenoxycarb will degrade in the soil environment under aerobic soil conditions. Under aerobic conditions, the half-life of fenoxycarb ranged from 60 to 106 days (or 2 to 3.5 months). Mineralization to CO₂ and metabolite (including Ro-16-8797 (ethyl[2-(p-(p-hydroxyphenoxy) phenoxy) ethyl] carbamate) and Ro 17-3192) binding to soils appears to be the primary means of dissipation in the soil environment. In a companion study (Pyrdé and Etterli, 00109331), fenoxycarb was stable in autoclaved soils incubated under aerobic conditions. Hence, EFGWB concludes that fenoxycarb degradation in aerobic soils is a microbially-mediated process including chemical incorporation into soil organic matter with subsequent biological oxidation to CO₂.

MATERIALS AND METHODS:

Chemical: Radiolabeled ¹⁴C-fenoxycarb (ethyl[2-(p-phenoxyphenoxy-1,4-¹⁴C)ethyl]carbamate), specific activity = 36.06 uCi/mg, radiochemical purity >98%, Unlabeled fenoxycarb.

Soils: Three Swiss soils (Commugny sandy loam, Dielsdorf sandy loam and Steinmaur loam). See Table O for soil characterizations.

Samples of the Swiss soils were fortified with 5 ppm ¹⁴C-fenoxycarb/unlabeled fenoxycarb. Moisture content of the soils was 25% of the maximum water capacity. Soils samples were maintained at

22° C in incubation flasks equipped with a trapping tower containing a polyurethane plug and granular soda lime to trap volatile radioactivity and $^{14}\text{CO}_2$.

At 0, 1, 2, 7, 14, 21 days and 1, 2, 3, 4, 6, 9, 12 months of incubation, soil samples were taken. Samples were extracted with acetonitrile/buffer extraction solvent. The buffer solution was further partitioned with ethyl acetate. Trapping towers were analyzed at 2 week intervals. Any $^{14}\text{CO}_2$ sorbed to the granular soda lime was released by adding HCl and retrapping the radioactivity in scintillation cocktail.

Radioactivity in all aliquots was quantitated with LSC. Unextracted soil radioactivity was quantitated by soil combustion with LSC of the liberated $^{14}\text{CO}_2$. Extracted radioactivity of the samples at 2 and 3 months incubation was analyzed for identity of degradation products. Analysis was by TLC and HPLC with co-chromatography with known standards.

REPORTED RESULTS:

The authors report that recovery of radioactivity in spiked control samples was 101.2%, of which 98.4% was extractable and 2.8% soil bound. Recovery of radioactivity at day 0 was 98.2%, 100.2% and 101.2% for the Commugny, Dielsdorf and Steinmaur soils, respectively. Recovery values decreased to 79.7%, 85.5% and 82.8% after 12 months incubation.

The authors report that in Commugny, Dielsdorf and Steinmaur soils the extracted radioactivity decreased from 95.75, 97.2% and 98.4% at day 0 to 12.8%, 23.7% and 16.3% after 12 months incubation. Total $^{14}\text{CO}_2$ during the 12 month incubation period was 26.5%, 21.9% and 23.3% for Commugny, Dielsdorf and Steinmaur soils, respectively. No other volatiles were found. The authors report that unextractable or bound residues increased with time of incubation. The amount of radioactivity remaining in soils (i.e., combusted) after 12 months incubation accounted for 42.3%, 43.2% and 46.3% of the applied radioactivity in the Commugny, Dielsdorf and Steinmaur soils, respectively (Tables I-III and Figures 4-6).

After 12 months incubation, extractable parent fenoxycarb accounted for 3%, 6%, and 14% of the applied radioactivity in the Commugny, Steinmaur and Dielsdorf soils, respectively. (At day 0, extractable parent fenoxycarb accounted for 93-98% of the applied radioactivity in the soils.) Extractable metabolite I (TLC $R_f > 0$) and metabolite II ($R_f = 0$) accounted for 1-8% of the applied radioactivity during the course of the study (Tables IV-VI).

HPLC analysis of the radioactivity extracted from soil incubated 2 and 3 months tentatively identified two degradation products, Ro-16-8797 (ethyl[2-(p-(p-hydroxyphenoxy)phenoxy)ethyl]carbamate) and Ro 17-3192, accounting for 1-3% of the applied radioactivity, as present

in the soils (Figure 7). Unidentified polar metabolites I and II (designated according to HPLC retention times), accounting for 1-7% of the applied radioactivity, were also found as shown Table VII.

Based on the results of the study, the authors report that half-lives of fenoxycarb were calculated to be 1.7, 2.3 and 2.5 months for Commugny, Steinmaur and Dielsdorf soils, respectively. The authors proposed that, along with the steady formation of CO₂, intermediate phenolic degradates of fenoxycarb were incorporated into the humic acid constituents of the soil. The authors proposed a degradation scheme with Ro 16-8797 and Ro 17-3192 as intermediates (Figure 7).

DISCUSSION:

The soils used in these studies are of Swiss origin; therefore, making an interpolation of fenoxycarb degradation in U.S soils difficult. Furthermore, there is no U.S.D.A. soil classification of the Swiss soils to permit interpolation of the soil properties to U.S soils. Future experiments would be more useful if conducted in U.S soils.

The soils were sieved to a less than 1.6 mm particle-size distribution and, therefore, very coarse sand (>1 mm particle-size) was removed from the soil likely changing the soil physical and chemical properties. EFGWB accepts this experimental protocol; however, future experiments should be conducted on soils sieved to less than a 2.0 mm particle-size distribution.

The soils were exposed to acetone (45 ml acetone/ 850 grams of soil) prior to incubation for the aerobic metabolism studies. Since fenoxycarb degradation appear to be microbially-mediated, EFGWB has concern if this amount of acetone will affect on soil microbial activity.

Note: The registrant submitted a sterile soil metabolism study (Pryde and Etterli, 00109332) in which ¹⁴C-fenoxycarb was incubated in Dielsdorf, Steinmaur, and Commugny soils for 28 days. The authors reported that fenoxycarb was stable in all soils. Only traces of degradation products were observed the soils.

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DATA EVALUATION RECORD

STUDY IDENTIFICATION:

Pyrde, A. and M. Etterli. 1982. Laboratory Leaching with ¹⁴C-Ro 13-5223/024. Report No. 041/2830. Maag Agrochemicals. (MRID No. 00109333).

TYPE OF STUDY: Mobility-Column Leaching

REVIEWED BY:

James Hetrick, Ph.D., Chemist
Review Section 1, EFGWB, EFED

Signature: *James G. Hetrick*
Date: 3-2-90

APPROVED BY:

Paul J. Mastradone, Ph.D., Section Chief
Review Section 1, EFGWB, EFED

Signature: *Paul J. Mastradone*
Date: MAR - 2 1990

CONCLUSIONS:

General: This study is scientifically sound but is considered to be supplemental. The soils used in these studies were insufficiently compared to U.S. soils. Furthermore, the soils used in these studies were sieved through a 0.8 mm sieve and, therefore, coarse and very coarse sand fractions were removed from the soil (USDA textural classification). Finely-sieved soil may impede pesticide mobility by decreasing the soil pore volume and increasing the effective soil colloid adsorption surface-area. In addition, distilled water was used as an eluent instead of a 0.1 M CaCl₂ solution. Eluent low in Ca²⁺ may cause dispersion of the soil particles (expansion of the soil colloid diffuse double layer) with subsequent constriction to water movement. Hence, EFGWB concludes that leaching data produced by these experimental procedures may underestimate fenoxycarb movement in soil.

Unaged Soil: The unaged leaching study is scientifically valid; however, the study is considered supplemental for the data requirements. Only two soils types are represented in the unaged leaching studies. More importantly, the unaged leaching study used only 40% (392 ml) of the required eluent to leach a 30 cm packed soil column. In addition, distilled water was used as an eluent instead of 0.1 M CaCl₂ solution.

Aged Soil: The aged-leaching study supplements the Subdivision M data requirements. Only one soil was used in this study and it was of foreign origin. As noted in the general discussion of the soil used in the aged-leaching studies were poorly compared to U.S. soils. Additionally, the soil in the aged-leaching study was eluted with distilled water instead of 0.01 M CaCl₂ solution.

Based on supplemental data provided in these studies, EFGWB concludes that fenoxycarb does not appear to be mobile under the conditions of the study conditions. Results of the aged-leaching study indicate that less than 3 % of the parent ^{14}C fenoxycarb moved beyond the 0-5 cm pesticide application zone. The aged-leaching study indicates that ^{14}C from radiolabelled fenoxycarb was predominately found in the eluent and soil column as unaltered parent fenoxycarb with trace quantities of unidentified degradates. Similarly, the unaged leaching studies (based on supplemental results) suggest that less than 1% of the parent fenoxycarb moved below the 0-5 cm pesticide application site.

MATERIALS AND METHODS:

Samples of two Swiss soils, Steinmaur and Wallis soils (see Table 0 for characteristics) sieved to 800 μm were added as a slurry to 5 cm diameter glass columns to a height of 30 cm. Excess water was allowed to drain from the column. Soil columns were fortified with ^{14}C -fenoxycarb (radiolabeled in the 1,4 carbon positions of the dioxyphenyl ring, specific activity = 36.06 $\mu\text{Ci}/\text{mg}$, radiochemical purity = >98%, chemical purity =>99%) equivalent to 0.876 kg/ha and immediately eluted with 393 ml of water (simulating a 20 cm rainfall) over a period of two days.

For aged residues, a sample of Steinmaur soil was fortified with ^{14}C -fenoxycarb to 5 ppm and aged under aerobic conditions for 30 days. After incubation, a soil sample was placed on a soil column similarly prepared as described above and eluted with 0.52 ha-cm (10.2 ml) of water for 40 days for total of 408 ml of water applied.

After elution of the water, the soil was extracted from the columns and sectioned into six 5 cm segments. The top 0-5 cm segment of soil was extracted using buffered acetonitrile solution then soxhlet extracted using acetonitrile. Radioactivity in the extraction phases (organic and aqueous) was quantitated by LSC. Tentative identification of extracted radioactivity was conducted with TLC. Soil bound (non-extracted) radioactivity was determined by combustion of soil sample and quantitating the CO_2 released.

REPORTED RESULTS:

The authors report that, for the unaged soil, recovery (material balance) ranged from 102.0% to 111.7% in the Steinmaur soil and from 114.6% to 118.5% in the Wallis soil. For the aged soil, recovery ranged from 93.7% to 100.1% of the column applied radioactivity in the Steinmaur soils.

The authors report that, in both the aged and unaged soil columns, all eluates and soil segments other than the top (0 to 5 cm) segment contained only traces (<1%) of the applied radioactivity for both Steinmaur and Wallis soils. In the aged residue soil column, 93.6%

of the applied radioactivity was located in the top 0 to 5 cm of the soil column (i.e., at the point of application) (Tables 1 and 2).

The majority of the soil extractable radioactive residues was present as unchanged Ro 13-5223. Fenoxycarb accounted for 50.1% and 80.6% of the applied radioactivity and extracted from the 0-5 cm column segment of the unaged Steinmaur and Wallis soils, respectively, and 56.8% of the applied radioactivity in the aged Steinmaur soil. Several unidentified degradation products were observed in trace amounts (Figures 1, 2, and 3).

Based on the results of the study, the authors concluded that both aged and unaged residues are strongly bound to typical loam and sandy loam soils and showed little or no tendency to leach.

DISCUSSION:

The soils used in these studies are of Swiss origin; therefore, making interpolation of fenoxycarb mobility in U.S. soils difficult to assess. Furthermore, there is no U.S.D.A. soil classification of the Swiss soils to permit interpolation of the soil properties to U.S. soils. Future experiments would be more useful if conducted in U.S. soils.

The soils were sieved to less than a 0.8 mm particle-size distribution and, therefore, the sand fractions were removed from the soil. EFGWB recognizes finely-sieved soil increases pesticide adsorption and eliminates any soil structural affect on soil pore-size distribution. Hence, EFGWB concludes the leaching data may underestimate the potential for fenoxycarb leaching. In future experiments, the soil should be sieved to < 2 mm to avoid altering the soil physicochemical properties.

The leachate samples contained straw-colored material lending evidence to movement of organic materials. The leachates, however, contained less than 1% of the parent fenoxycarb applied to the soil column leaching cylinder. EFGWB concludes that fenoxycarb and degradates do not appear to be integrally associated with the soluble soil organic matter fraction.

The eluant did not contain Ca^{+2} to promote flocculation of soil particles. EFGWB recognizes the column leaching studies may underestimate fenoxycarb leaching potential due to soil particle dispersion. Future leaching experiments should use an eluant with at least a 0.01 M Ca^{+2} concentration.

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DATA EVALUATION RECORD

STUDY IDENTIFICATION:

Pyrde, A. and M. Etterli. 1982. Freundlich Adsorption and Desorption constants for ^{14}C -Ro 13-5223/024 in Four Soils. Report No. 041.2674. Maag Agrochemicals. (MRID No. 00109333).

TYPE OF STUDY: Leaching - Adsorption/desorption

REVIEWED BY:

James Hetrick, Ph.D., Chemist
Review Section 1, EFGWB, EFED

Signature: *James G. Hetrick*
Date: 3-2-90

APPROVED BY:

Paul J. Mastradone, Ph.D., Section Chief
Review Section 1, EFGWB, EFED

Signature: *Paul J. Mastradone*
Date: 3-2-90

CONCLUSIONS:

This study is considered supplemental and does not fulfill the data requirement for adsorption/desorption studies. The soils used in these studies were finely-sieved ($< 0.5\text{ mm}$); therefore, the adsorption surface area (based on soil mass) of the soil will be higher than soil sieved through a 2 mm sieve (See discussion section). In addition, the distilled water rather than a 0.01 M Ca^{+2} solution as the equilibration matrix.

Based on supplemental data, parent fenoxycarb has a moderate to strong soil binding affinity (K_d 17 to 77) to soil particles rendering it immobile in the soil. Similarly, the column leaching studies (Pyrde and Etterli, 00109331) indicates that parent fenoxycarb and degradates did not leach beyond the pesticide application site.

MATERIALS AND METHODS:

Stock solutions of ^{14}C -fenoxycarb (specific activity = 36.06 uCi/mg , radiochemical purity $\Rightarrow 98\%$, chemical purity $\Rightarrow 99\%$) were prepared in distilled water at 0.099, 0.29, 1.19 and 1.3 ppm. Aliquots of the stock solutions were added to triplicate samples of four Swiss soils (Dielsdorf, Steinmaur, Commugny and Wallis soils, Table 0 for characteristics) and shaken for 24 hours at 20°C . Solutions were then centrifuged and aliquots of the supernatant were taken. Radioactivity in the supernatant was quantitated by LSC. Desorption constants were determined by re-suspending the centrifuged soil in distilled water or saturated calcium sulfate solution. Freundlich adsorption (and desorption) coefficients were calculated based on the amount of radioactivity adsorbed to the soil particles.

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Pages 30 through 41 are not included.

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REPORTED RESULTS:

The authors reported Freundlich adsorption constants of 49, 77 and 77 for the heavier Dielsdorf, Steinmaur and Commugny soils and 18 for the lighter Wallis soil. Desorption values for the distilled water were 73, 98, and 125 for the Dielsdorf, Steinmaur and Commugny soils, respectively, and 24 for the Wallis soil. The desorption values for the saturated calcium sulfate solution were somewhat less (Tables 1-9).

The authors reported that fenoxycarb has moderate adsorption to lighter soils (Wallis, organic matter content = 1.4%, adsorption K value of 17) and strong adsorption to heavier soils (Dielsdorf, Steinmaur and Commugny soils where organic matter = >2%, adsorption K values ranging from 49 to 77).

The authors concluded that fenoxycarb would be strongly adsorbed to most agricultural soils.

DISCUSSION:

The soils were sieved to a less than 0.5 mm particle-size distribution and, therefore, the coarse sand fractions were removed from the soil. EFGWB recognizes finely-sieved soil increases pesticide adsorption by concentrating the soil exchange capacity and increased surface area (based on a soil mass). Hence, EFGWB concludes the adsorption/desorption data may overestimate the potential for fenoxycarb binding to soil. In future experiments, the soil should be sieved to < 2 mm to avoid altering the soil physicochemical properties.

The use of distilled water as an equilibration matrix prevents control of the "soil solution" ionic strength; therefore, the ionic strength of the equilibration matrix is controlled by mineral dissolution kinetics and cation exchange mechanisms. The lack of control on the soil solution ionic strength may prevent pesticide-colloid equilibration due to alteration of ion activities.

DATA EVALUATION RECORD

STUDY IDENTIFICATION:

Pyrde, A. and M. Etterli. 1982. Freundlich Adsorption and Desorption constants for ^{14}C -Ro 13-5223/024 in Four Soils. Report No. 041.2674. Maag Agrochemicals. (MRID No. 00109333).

TYPE OF STUDY: Leaching - Adsorption/desorption

REVIEWED BY:

James Hetrick, Ph.D., Chemist
Review Section 1, EFGWB, EFED

Signature: *James G. Hetrick*
Date: 3-2-90

APPROVED BY:

Paul J. Mastradone, Ph.D., Section Chief
Review Section 1, EFGWB, EFED

Signature: *Paul J. Mastradone*
Date: MAR - 2 - 1990

CONCLUSIONS:

This study is considered supplemental and does not fulfill the data requirement for adsorption/desorption studies. The soils used in these studies were finely-sieved ($< 0.5\text{ mm}$); therefore, the adsorption surface area (based on soil mass) of the soil will be higher than soil sieved through a 2 mm sieve (See discussion section). In addition, the distilled water rather than a 0.01 M Ca^{+2} solution as the equilibration matrix.

Based on supplemental data, parent fenoxycarb has a moderate to strong soil binding affinity (K_d 17 to 77) to soil particles rendering it immobile in the soil. Similarly, the column leaching studies (Pyrde and Etterli, 00109331) indicates that parent fenoxycarb and degradates did not leach beyond the pesticide application site.

MATERIALS AND METHODS:

Stock solutions of ^{14}C -fenoxycarb (specific activity = 36.06 uCi/mg , radiochemical purity $\geq 98\%$, chemical purity $\geq 99\%$) were prepared in distilled water at 0.099, 0.29, 1.19 and 1.3 ppm. Aliquots of the stock solutions were added to triplicate samples of four Swiss soils (Dielsdorf, Steinmaur, Commugny and Wallis soils, Table 0 for characteristics) and shaken for 24 hours at 20°C . Solutions were then centrifuged and aliquots of the supernatant were taken. Radioactivity in the supernatant was quantitated by LSC. Desorption constants were determined by re-suspending the centrifuged soil in distilled water or saturated calcium sulfate solution. Freundlich adsorption (and desorption) coefficients were calculated based on the amount of radioactivity adsorbed to the soil particles.

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REPORTED RESULTS:

The authors reported Freundlich adsorption constants of 49, 77 and 77 for the heavier Dielsdorf, Steinmaur and Commugny soils and 18 for the lighter Wallis soil. Desorption values for the distilled water were 73, 98, and 125 for the Dielsdorf, Steinmaur and Commugny soils, respectively, and 24 for the Wallis soil. The desorption values for the saturated calcium sulfate solution were somewhat less (Tables 1-9).

The authors reported that fenoxycarb has moderate adsorption to lighter soils (Wallis, organic matter content = 1.4%, adsorption K value of 17) and strong adsorption to heavier soils (Dielsdorf, Steinmaur and Commugny soils where organic matter = >2%, adsorption K values ranging from 49 to 77).

The authors concluded that fenoxycarb would be strongly adsorbed to most agricultural soils.

DISCUSSION:

The soils were sieved to a less than 0.5 mm particle-size distribution and, therefore, the coarse sand fractions were removed from the soil. EFGWB recognizes finely-sieved soil increases pesticide adsorption by concentrating the soil exchange capacity and increased surface area (based on a soil mass). Hence, EFGWB concludes the adsorption/desorption data may overestimate the potential for fenoxycarb binding to soil. In future experiments, the soil should be sieved to < 2 mm to avoid altering the soil physicochemical properties.

The use of distilled water as an equilibration matrix prevents control of the "soil solution" ionic strength; therefore, the ionic strength of the equilibration matrix is controlled by mineral dissolution kinetics and cation exchange mechanisms. The lack of control on the soil solution ionic strength may prevent pesticide-colloid equilibration due to alteration of ion activities.

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DATA EVALUATION RECORD

STUDY IDENTIFICATION:

Ellgehausen, H. 1985. Accumulation and Elimination of ^{14}C -Ro 13-5223/024 by Bluegill Sunfish in a Dynamic Flow Through System (MRID No. 00148191).

TYPE OF STUDY: Fish accumulation study

REVIEWED BY:

Akiva D. Abramovitch, Ph.D., Chemist
Review Section 1, EFGWB, EFED

APPROVED BY:

Samuel Creeger, Section Chief
Review Section 1, EFGWB, EFED

COMPILED BY:

James A. Hetrick, Ph.D., Chemist
Review Section 1, EFGWB, EFED

Signature: *James A. Hetrick*
Date: 3-2-90

CONCLUSIONS:

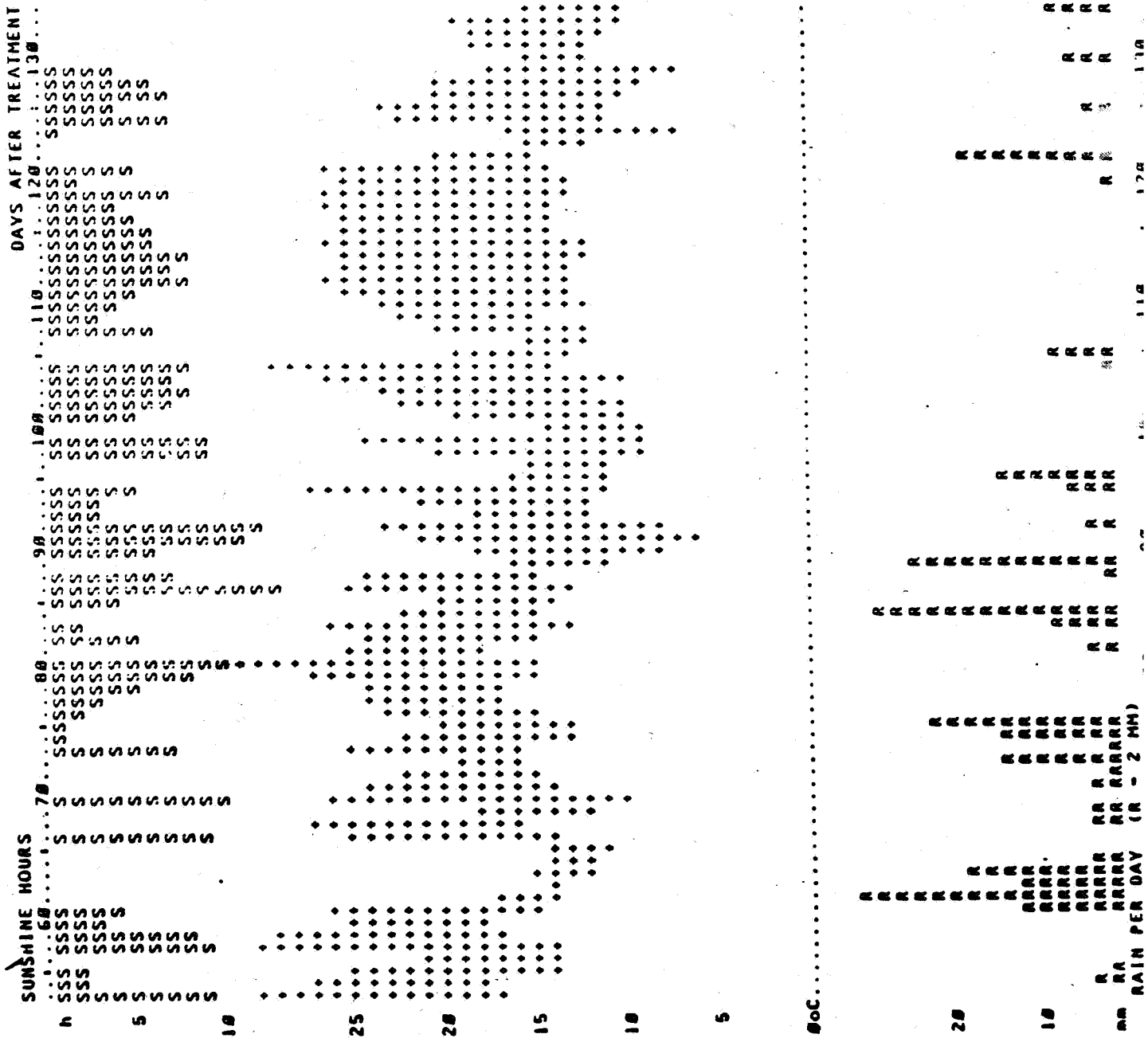
Based on the combined results of this study and study (Ellgehausen, 00148191), EFGWB accepts the fish accumulation studies fulfill the data requirements. The data submitted indicated the bioaccumulation factor for fenoxycarb was 277.6 (whole fish), 138.9 (edibles), and 439.6 (non-edibles) but 99.0, 98.1, and 98.4% of the initially accumulated organic material was eliminated in a two week depuration. Most of the residual material (94%) in the edible portion was the parent Ro 13-5223. The non-edible portion contained in addition to the parent compound (64%), some polar degradates of which hydroxylated metabolites were positively identified.

MATERIALS AND METHODS:

The study was conducted with a ^{14}C radiolabelled Ro 13-5223/024 of a specific radioactivity of $36.06 \text{ uCi mg}^{-1}$ and 98% radiochemical purity. This material was mixed with unlabeled active ingredient resulting in a specific activity of $0.832 \text{ uCi mg}^{-1}$. The flow through system contained three individual water tanks containing 100 liters of water. Two tanks received 150 fish each and the control tank 50 fish. The fish (average weight of 3 gm) were acclimated for four weeks prior to experimentation and during that period only 0.6% mortality was observed. The temperature was maintained at 20°C ($19.5\text{--}20.0^\circ\text{C}$) throughout the experiment. The pH and the temperature,

APPENDIX 1 Weather data during trial (page v)

(DAT = days after treatment)



were recorded when the samples were taken at days 0, 1, 3, 7, 14, 21 and 28 of the exposure period and 7.4-8 and the oxygen concentration averaged 7.4 mg L⁻¹. Samples of 15 fish were taken at the specified time intervals. Additional fish (12-30) were taken for future analysis of metabolites. Control fish were taken at the specified time intervals. Additional fish were taken for future analysis of the metabolites. Control fish were taken for analysis at days 0 and 28. The fish samples were separated into edible and non-edible portions and homogenized. Aliquots of the homogenized fish samples were placed in 25 ml glass scintillation vials and 2.0 ml of tissue solubilizer was added and incubated at 50°C for 24 hours. Then 20 ml of scintillation mixture were added and the radioactivity was determined. For control purposes, the radioactivity in various samples was also determined also by combustion. Water samples were extracted with chloroform and analysed on TLC plates in reference to authentic samples of Ro-5223/024 and potential metabolites.

REPORTED RESULTS:

The accumulation in fish reached a plateau in about 7 days and reached values of 77.04+/-8.38 mg kg⁻¹ for the whole fish, 38.52 +/- 4.8 mg kg⁻¹ for the edible parts and 121.99 +/-25.6 mg kg⁻¹ for the non-edible parts. A bioaccumulation factor of 277.6, 138.9, and 439.6 was not obtained for the whole fish, edible and non-edible parts, respectively. Depuration was fast within the initial 7 days and the residual radioactivity dropped to 1.5, 2.4, and 2.1% of their plateau values for the edible, non-edible and whole fish, respectively. The elimination rate of residual radioactivity can be described by a second order reaction kinetics. Based on the octanol/water partition coefficient, a value of 277, the registrant calculated a BCF value of 69.6 based on log=4.28 and the formula $\log BCF = 0.83 \times \log P - 1.71$.

DISCUSSION:

Based on the 28 day data, BCF of 163, 572, and 319 were obtained in the edibles, non-edibles, and whole fish, respectively.

For added clarity the two fish accumulation studies should have been combined into one study. Furthermore, EFGWB disagree with author's position that the accumulation plateau was reached at 7 days (it appears that accumulation was still occurring when exposure was at 28 days).

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DATA EVALUATION RECORD

STUDY IDENTIFICATION:

Ellgehausen, H. 1985. Nature of Radioactive Residues in 14C-Ro 13-5223/024 - Treated Bluegill Sunfish (MRID No. 00148191).

TYPE OF STUDY: Fish accumulation study

REVIEWED BY:

Akiva D. Abramovitch, Ph.D., Chemist
Review Section 1, EFGWB, EFED

APPROVED BY:

Samual M. Creeger, Section Chief
Review Section 1, EFGWB, EFED

COMPILED BY:

James A. Hetrick, Ph.D., Chemist
Review Section 1, EFGWB, EFED

Signature: *James G. Hedrick*
Date: 3/2/90

CONCLUSIONS:

Based on the results of this study and previous studies (Ellgehausen, 00148191), EFGWB considers the data requirement for the fish accumulation study fulfilled. The data submitted indicated that the bioaccumulation factor for Ro 13-5223 was 277.6 (whole fish), 138.9 (edibles), and 439.6 (non-edibles) but 99.0, 98.1, and 98.4% of the initially accumulated organic material was eliminated in a two week depuration. Most of the residual material (94%) in the edible portion was the parent Ro 13-5223. The non-edible portion contained in addition to the parent compound (64%), some polar degradates of which hydroxylated metabolites were positively identified. Based on the low use rates associated with the proposed fire ant bait use, potential for impact on aquatic systems and accumulation by aquatic organisms is low.

MATERIALS AND METHODS:

Fish samples that were removed after 21 and 28 days of exposure were separated into edible and non-edible portions and homogenized. Aliquots were combusted to determine the total amount of radioactivity. Other portions were extracted with chloroform in a Soxhlet for 24 hours, the chloroform was evaporated to dryness and the residue was then dissolved in hexane (100 ml) and partitioned into acetonitrile (100 ml). Additional extraction was accomplished

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with methanol/water (3:1).

REPORTED RESULTS:

Ninety-nine percent of the accumulated radioactivity in the edible sample was extracted with chloroform, the remainder 4.1% with methanol/water (3:1) and unextracted residues (2.1%) were accounted by combustion for a total of 105%. Ninety-six percent of the radioactivity in the chloroform extract, was found in the acetonitrile and 5.5% in the hexane for a total of 101.5%. Analysis of the acetonitrile phase by HPLC indicated that 94.5% of the radioactivity initially accumulated in the edible sample was the parent compound (Ro 13-5223). Radioactivity recoveries of 73.7% were found in the chloroform extract indicated that it contained 63% of the radioactivity initially found in the parent compound and 18.5% of the accumulated radioactive material were fast eluting polar compounds. The major polar degradates identified was Ro 16-8797 (3.9%). Other polar degradates were not identified.

DISCUSSION:

Based on the 28 day data, BCF of 163, 572, and 319 were obtained in the edibles, non-edibles, and whole fish, respectively.

For added clarity the two fish accumulation studies should have been combined into one study. Furthermore, EFGWB disagree with author's position that the accumulation plateau was reached at 7 days (it appears that accumulation was still occurring when exposure was at 28 days).

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DATA EVALUATION RECORD

STUDY IDENTIFICATION:

A. Pryde and M. E. Herli. 1982. Ro 13-5223/024 (¹⁴C) Bioaccumulation Factor and Metabolism Study in Fish as the Fire Ant Bait ACR-2913. Accession No. 041-3489.

TYPE OF STUDY: Fish accumulation study

REVIEWED BY:

Richard V. Moraski, Ph.D., Chemist
Review Section 1, EAB, HED

APPROVED BY:

Samual M. Creeger, Section Chief
Review Section 1, EFGWB, EFED

COMPILED BY:

James A. Hetrick, Ph.D., Chemist
Review Section 1, EFGWB, EFED

Signature:
Date:

CONCLUSIONS:

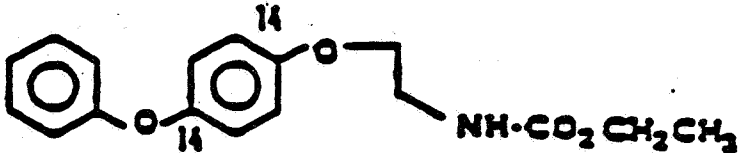
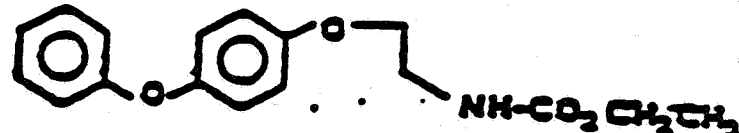
The study is scientifically valid; however, the study does not meet the Subdivision M guidelines. The fish accumulation study was conducted using a static exposure system. EFGWB does not accept static accumulation studies due to the possibility of improper tank mixing of the pesticide solution. EFGWB concludes the study provides supplemental data for the fish accumulation data requirement.

Radiolabelled fenoxycarb (Ro 13-5223/024) appears to have an approximate bioaccumulation factor of 95. In contrast, a companion fish accumulation study (Ellgehausen, 00148191) report a whole-fish fenoxycarb bioaccumulation factor of 277. Therefore, EFGWB concludes that fenoxycarb has a bioaccumulation factor between 100 to 277.

MATERIALS AND METHODS:

A static fish accumulation study was conducted using aquarium water spiked with 0.152 ug/ml of fenoxycarb. The species of fish used was the bitterling. Forty-six fish were placed in the aquarium; 5 were removed and sampled daily. Samples were taken during the first 4 days. Radioactivity was measured by combustion analysis. During depuration phase, samples were taken on days 1, 3, 6, 11, and 17.

Table 1: Structure of the test compound.

Designation	Structure
^{14}C -Ro 13-5223/024	
Ro 13-5223/000	

depuration phase, samples were taken on days 1, 3, 6, 11, and 17. Metabolite identification was conducted using GC-MS and HPLC.

REPORTED RESULTS:

Using HPLC, radio GC-MS, no unchanged fenoxycarb was recovered from depuration water. Metabolites were present in low quantities. One metabolite was identified as 4,4'-dihydroxybiphenyl ether. A sample of the aquarium water after 4 days accumulation period indicated no parent fenoxycarb was present. Table 1 gives results of accumulation and depuration phases. An approximate bioaccumulation factor of 95 was calculated.

DISCUSSION:

The study was reviewed (11/28/84) and is considered supplemental to fulfilling the fish accumulation data requirements. The fish accumulation study is considered to be a supplemental study because it was conducted in a static system. EFGWB recognizes that a static fish study may invoke pesticide concentration gradients due to improper mixing.

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