CASE GS -- PP321 STUDY 5 PM --

CHEM -- PP321

BRANCH EAB DISC --

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID No MRID CONTENT CAT 01

Hamer, M.J. and I.R. Hill. 1985. The accumulation of cyhalothrin and its degradation products by channel catfish and Daphnia magna in a soil/water system. RJ 0427B. Prepared and submitted by ICI Americas, Inc., Wilmington, DE. Acc. No. 470082-034.

SUBST. CLASS = S.

DIRECT RVW TIME = 16 (MH) START-DATE END DATE

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This cyhalothrin study was submitted to support the registration of PP321.

CONCLUSION:

Laboratory Accumulation - Fish

1. This study is scientifically sound and provides supplemental data on the laboratory accumulation of PP321 in fish.

2. In a static sediment/water exposure system, where loamy sand soil was treated with [^{14}C]cyhalothrin (radiochemical purity 96.6%) at 50 g ai/ha, aged 21 days, and flooded, total radioactivity accumulated slightly in channel catfish with maximum bioconcentration factors of 7x in edible tissues, 66x in nonedible tissues, and 19x in whole fish by day 14 of a 31-day exposure period. Radioactivity in the water increased from 0.28 ppb at day 0 to 0.95 ppb at day 32 of the exposure period.

3. This study does not fulfill EPA Data Requirements for Registering Pesticides because a flow-through system was not used, the fish were not exposed to a constant concentration of pesticide, the concentrations of degradates were unacceptably high, the residues in the water and fish

were not characterized, the registrant did not prove that the activity of cyhalothrin in a biological system was equivalent to that of PP321, and the uptake, bioaccumulation, and depuration of PP321 were not specifically addressed and reported.

MATERIALS AND METHODS:

Channel catfish (Ictalurus punctatus, average length and weight 102 mm and 11.6 g, respectively) were held in culture tanks for 7 weeks under unspecified conditions during which no disease-related mortalities were observed prior to the initiation of the study. Static water/sediment exposure systems were prepared using two stainless steel cylinders (200-cm wide x 60-cm deep). Cyclopropane-labeled [^{14}C]cyhalothrin (specific activity 1.9 GBq/mMol; total radiochemical purity 96.6% consisting of 1.2% trans-isomers and the enantiomeric pairs A' [3.4%], A [56%], B' [2.8%], and B [36.7%]; Jealott's Hill Research Station, U.K.) in acetone was thoroughly incorporated into loamy sand soil (36% coarse sand, 44% fine sand, 10% silt, 10% clay, 1.7% organic matter, CEC 6.6 meq/100 g, pH 5.2, moisture-holding capacity at zero suction 34) at a concentration of 50 g ai/ha. One cylinder was filled with the treated soil to a depth of 3 cm; the other cylinder was filled similarly with untreated control soil. Soil samples were immediately analyzed to determine the exact concentration of radioactivity. The soil was kept moist by watering and was incubated at "ambient" temperatures under a 16-hour photoperiod with fluorescent lighting combined with natural light. Samples were collected at intervals for up to 21 days.

After 21 days of aging, the soils were flooded with 1400 L of tap water (temperature 18-20°C, dissolved oxygen 8.7 mg/L, hardness 204-316 mg/L, alkalinity 240-355 mg/L, specific conductivity 530-846 µS/cm, un-ionized ammonia <0.004-0.05 mg/L nitrogen, residual chlorine <0.05 mg/L, copper <0.02-0.35 mg/L, lead, zinc and fluoride each <0.12 mg/L); the water and soil were sampled and left to equilibrate for 3 days. Following equilibrium, the water and soils were sampled, and 150 channel catfish were introduced into the system. Fish were maintained on a diet of dry pellet food (Promin, coarse; Promin Ltd.) daily. The water was continuously aerated. After 21 days of exposure, 60 fish from each cylinder were placed in separate glass aquaria containing flowing, aerated, dechlorinated, filtered water (characteristics as above with the exception of dissolved oxygen >5 mg/L and temperature 17-22°C) for a 42-day depuration period. Fish and water were sampled on days 1, 3, 7, 14, 21, and ~31 of the exposure period, and days 1, 3, 7, 14, 31, and 42 of the depuration period. Soil was sampled at intervals up to 32 days (1 day beyond the fish were exposed) of exposure.

Soil samples were sequentially extracted with acetonitrile followed by acetonitrile:water (70:30). Total radioactivity in the extracts and extracted soil was determined by LSC and LSC following combustion, respectively. The extracts were combined and concentrated. Aliquots were analyzed for total radioactivity by LSC and for degradates by TLC with reference compounds. TLC was performed using unspecified plates developed with cyclohexane saturated with formic acid:diethyl ether (3:2). Reference standards were located with UV light and by spraying

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the chromatograms with a solution of bromophenol blue in acetone. Radioactive areas were located by autoradiography and quantified using a TLC linear analyzer.

Total radioactivity in water was determined using LSC. Aliquots of water samples from days 1, 7, 21, 28 and 31 of the exposure period were extracted with hexane to remove parent cyhalothrin, acidified to pH 1 with 10 M HCl, and extracted once more with diethyl ether. Aliquots of the water, ether and hexane fractions were measured for radioactivity using LSC. The other fraction was dried over anhydrous sodium sulfate, concentrated, and analyzed using TLC as described above for soil. The hexane fraction did not contain sufficient radioactivity to warrant TLC analysis.

Pooled samples of whole fish (3) and pooled samples (4) of edible (lateral musculature, skin and bones) and nonedible (viscera) tissues were wet-weighed, frozen, and analyzed for radioactivity by LSC following combustion.

REPORTED RESULTS:

[^{14}C]Residues in the water gradually increased from 0.28 ppb at 0 days of exposure to 0.95 ppb at 32 days of exposure (Table 1). Parent cyhalothrin concentrations were reported to be <0.003 ppb. (1RS)-cis-3-(ZE-2-Chloro-3,3,3-trifluoroprop-1-enyl)-2,2-dimethylcyclopropanecarboxylic acid (Ia) was reported to constitute up to 5.3% of the "applied" radioactivity in water (see Discussion point 4). Maximum accumulation of [^{14}C]residues in fish occurred by day 14 of the exposure period with bioconcentration factors of 7x in edible tissue (3.6 ppb), 66x in nonedible tissues (33.8 ppb), and 19x in whole fish (9.6 ppb) (Table 1). Residues depurated quickly reaching concentrations of 1.3, 1.0, and 1.0 ppb in edible, nonedible, and whole fish, respectively, after 42 days. [^{14}C]Residues in the soil decreased from 110.7% of the applied on the day of treatment, to 47% of the applied at day 0 of the exposure to fish (3 days after the soil was flooded) (Table 2). Over 80% of the applied radioactivity was unaccounted for. (Table 2).

DISCUSSION:

1. The uptake, bioaccumulation, and depuration of PP321 were not specifically addressed and reported. The registrants did not prove that the activity of cyhalothrin in a biological system was equivalent to the activity of PP321.

2. A flow-through system was not used during the exposure period. Fish were exposed to varying concentrations of cyhalothrin residues released from aged treated soil rather than to constant concentrations of [^{14}C]-cyhalothrin. Reported BCF's differ greatly from those determined for flow-through methods.

3. Residues in the fish tissues were not characterized.

4. The concentrations of [^{14}C]degradates in water were presented as "% of the applied". Since the original treatment was made to soil, the data

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depicting water concentrations expressed as the percent of material applied to the soil is meaningless and cannot be analyzed without appropriate raw data expressed as ppb. Furthermore, only 5.3% "of the applied" was identified, thus, residues in water were not sufficiently characterized.

5. Soil TLC analysis failed to recover >80% of the radioactivity applied to the plate.

6. The type of plate used for TLC analysis (e.g., silica gel) was not specified.

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Table 1. Total radioactivity (ppb) in the water and tissues of channel catfish treated with cyclopropyl-labeled [^{14}C]cyhalothrin (radiochemical purity 96.6%) during a 31-day exposure period and 48-day depuration period.

Sampling interval (days)		Water	Edible[a]		Nonedible[b]		Whole fish	
			ppb	BCF[c]	ppb	BCF[c]	ppb	BCF[c]
Exposure	-3	0.04	--	--	--	--	--	--
	-2	0.09	--	--	--	--	--	--
	0	0.28	--	--	--	--	--	--
	1	0.34	0.7	2	6.9	20	5.8	17
	3	0.36	1.0	3	10.1	28	2.4	7
	7	0.38	2.2	6	17.0	45	3.7	10
	14	0.51	3.6	7	33.8	66	9.6	19
	21	0.65	3.1	5	18.6	28	6.8	10
	28	0.84	5.7	7	41.7	49	6.7	8
	31	--	6.5	7	45.5	48	8.4	9
	32	0.95	--	--	--	--	--	--
Depuration	1	--	6.8	105	27.2	60	6.7	80
	3	--	4.3	66	24.2	53	5.3	64
	4	--	--	--	--	--	5.1	61
	7	--	3.3	51	1.9	4	3.2	38
	14	--	2.1	32	1.8	4	3.1	37
	21	--	2.0	31	2.7	6	2.3	27
	42	--	1.3	20	1.0	2	1.0	14

[a] Lateral musculature, skin, and bones.

[b] Viscera.

[c] Bioconcentration factors for the exposure period are calculated by dividing the concentration of [^{14}C]residues in wet tissues by the concentration of [^{14}C]residues in water. Bioconcentration factors for the depuration period are calculated as a percentage of the [^{14}C]residues present on the last day of exposure in each of the tissues.

Table 2. Distribution of radioactivity (% of applied) in loamy sand soil treated with cyclopropane-labeled [^{14}C]cyhalothrin, incubated for 21 days, and flooded with aerated tap water for 32 days.

Sampling interval (days)		Total	Acetonitrile extract[a]					Isomeric composition[b]				
			Total	Ia[c]	XV[d]	Origin	Unidentified	A'	A	B'	B	Trans-isomers
Incubation	0	110.7	107.7	<1	<1	<1	1	4.0	60.4	3.1	39.4	0.7
	7	86.1	50.4	5	5	4	1	1.3	26.0	1.4	21.1	0.6
	14	75.7	34.6	4	7	2	1	0.9	15.3	1.0	16.8	0.6
	21	67.2	23.6	4	7	4	2	0.5	10.7	0.6	11.0	0.8
Exposure	0	47.4	13.5	2	4	3	1	0.4	5.6	0.4	6.8	0.4
	3	55.8	14.9	3	6	6	<1	0.3	6.6	0.3	7.3	0.3
	7	49.7	16.0	2	4	3	<1	0.5	7.3	0.5	7.5	0.3
	14	47.6	16.8	2	1	<1	<1	0.5	7.5	ND[b]	8.3	0.6
	28	50.2	13.6	6	2	3	<1	0.3	6.5	ND	6.4	0.4
	32	64.0	26.7	3	3	5	2	0.7	13.8	0.4	11.3	0.5

[a] As determined by TLC analysis.

[b] As determined by HPLC analysis: Isomer A' - E (1R) cis (R) α -CN cyhalothrin and E (1S) cis (S) α -CN cyhalothrin.
Isomer A - Z (1R) cis (R) α -CN cyhalothrin and Z (1S) cis (S) α -CN cyhalothrin.
Isomer B' - E (1R) cis (S) α -CN cyhalothrin and E (1S) cis (R) α -CN cyhalothrin.
Isomer B - Z (1R) cis (S) α -CN cyhalothrin and Z (1S) cis (R) α -CN cyhalothrin.

[c] (1RS)-cis-3-(ZE-2-Chloro-3,3,3-trifluoroprop-1-enyl)-2,2-dimethylcyclopropanecarboxylic acid.

[d] (RS)-α-Cyano-3-(4-hydroxyphenoxy)benzyl (1RS)-cis-3-(Z-2-chloro-3,3,3-trifluoroprop-1-enyl)-2,2-dimethylcyclopropanecarboxylate.

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