Shaughnessy No.: 125401

Date Out EAB: 23 NOV 1984

TO: R. Taylor
Product Manager # 25
Registration Division
TS-767

FROM: Samuel Creeger, Chief
Review Section No. 1
Exposure Assessment Branch
Hazard Evaluation Division

Attached please find the environmental fate review of:

Reg./File No.: 279-GNLE, -GNLG and -GNLU

Chemical: FMC 57020

Type Product: Herbicide

Product Name: COMMAND

Company Name: FMC

Submission Purpose: Registration of technical and products

ZBB Code: 3(c)(5)

Action Code: 105

Date In: 8/9/84

EAB # 4486-4488

Date Completed: 11/21/84

TAIS (Level II)	Days
61	19

Deferrals To:

______ Ecological Effects Branch

______ Residue Chemistry Branch

______ Toxicology Branch

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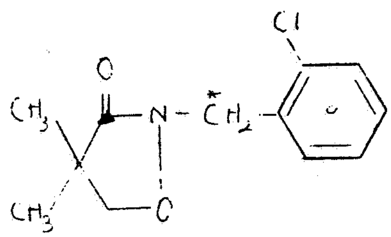
1.0 INTRODUCTION

FMC Corporation has submitted environmental fate data on Command® herbicide to support registration of technical and end-use products for use on soybeans.

1.1 Chemical - technical product

Chemical name: 2-(2-chlorophenyl)methyl-4,4-dimethyl-3-isoxazolidinone
Common name: dimethazone (proposed)
Trade name: Command
Company code number: FMC 57020
Molecular formula: $C_{12}H_{14}ClNO_2$
Structural formula:



° Ring-^{14}C-FMC 57020
* Methylene-^{14}C-FMC 57020
▲ Carbonyl-^{14}C-FMC 57020

Molecular Wt: 239.7

1.2 Physical and Chemical Characteristics

A copy of a summary is appended.

2.0 DIRECTIONS FOR USE

A copy of draft label for each of proposed products (Command Technical, Command 4EC and Command 6EC) is appended.

3.0 DISCUSSION OF DATA

3.1 Photodegradation of FMC 57020 in Water. J. Wu, FMC Corp. P-0869, 5/11/84, Notebook Rf. E2743, E1539, EPA. Acc. No. 072819 (Rf. 2)

<u>Experimental</u>

^{14}C-Labeled FMC 57020 (ring-^{14}C, 0.48 mCi/mmol, 99.3% pure; methylene-^{14}C, 0.27 mCi/mmol, 98.5% pure) was subjected to photolysis under natural sunlight or simulated sunlight (light source, a 275 W G.E. sunlamp, a description of the spectral energy distribution is on the following page) in the absence or presence of acetone (0.1 or 2.0% v/v).

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APPENDIX E

TABLE II. Ultraviolet spectral energy distribution of light sources. (Values are in μw/cm²/30-A band.)

Wave-length in A	Sunlight [illegible]	Sunlight [illegible]	Sunlight [illegible]	Sunlight [illegible]	Xenon	Xenon filtered	Xenotest	Fade-ometer	Sunlamp S-1	*Sunlamp RS	Mercury arc AH5	Mercury arc AH6	Fluores. black light	Fluores. black light filtered	Fluores. daylight	Fluores. sunlamp	Projection lamp	Purple X	Hydrogen arc Pyrex pipe	Hydrogen arc Vycor
2660	...	...	...	...	0.9	...	...	...	1.1	3.8	14.7	[illegible]	...	...	...	...	...	...	0.61	1.10
2690	...	...	...	...	1.1	...	...	...	0.7	2.8	9.2	[illegible]	...	...	...	...	...	...	0.59	1.09
2720	...	...	...	...	1.4	...	...	...	0.6	2.0	8.2	[illegible]	...	...	...	...	...	...	0.58	1.08
2750	...	...	...	...	[illegible]	...	...	1.8	0.9	3.9	8.2	11.6	...	...	...	...	...	...	0.56	1.06
2780	...	...	...	...	[illegible]	...	...	1.8	0.8	4.0	[illegible]	17.1	...	...	...	...	...	...	0.51	[illegible]
2810	...	...	...	...	[illegible]	...	...	2.0	3.9	[illegible]	11.5	21.3	...	...	...	...	...	0.01	0.51	1.03
2840	...	...	...	...	7.9	...	...	[illegible]	0.7	[illegible]	7.6	[illegible]	...	...	...	0.9	...	0.08	0.51	1.01
2870	...	...	...	...	9.3	...	...	[illegible]	0.7	[illegible]	6.0	[illegible]	...	...	...	...	...	0.08	[illegible]	0.98
2900	...	...	...	...	15.4	1.30	...	[illegible]	[illegible]	[illegible]	11.2	27.3	0.5	...	...	7.3	0.1	0.09	[illegible]	[illegible]
2930	...	0.08	0.10	0.03	21.1	3.32	...	3.3	2.1	[illegible]	7.0	[illegible]	0.3	...	...	[illegible]	0.1	0.10	[illegible]	[illegible]
2960	0.04	0.10	[illegible]	0.06	25.6	5.50	...	3.3	18.2	61.9	[illegible]	[illegible]	[illegible]	...	...	15.3	0.1	0.11	0.15	0.90
2990	0.12	[illegible]	[illegible]	0.10	30.7	8.61	...	3.0	16.1	61.3	[illegible]	[illegible]	1.0	0.6	...	[illegible]	0.2	0.12	[illegible]	[illegible]
3020	0.38	[illegible]	[illegible]	[illegible]	35.1	12.8	[illegible]	4.3	46.0	161	[illegible]	[illegible]	1.0	0.8	...	22.9	0.2	0.17	0.42	[illegible]
3050	1.03	[illegible]	[illegible]	[illegible]	[illegible]	18.9	13.0	3.0	3.6	[illegible]	[illegible]	36.0	1.3	0.7	...	25.3	0.3	0.18	0.40	0.80
3080	1.90	10.3	13.0	[illegible]	[illegible]	16.3	21.3	3.3	1.6	31.2	[illegible]	[illegible]	1.3	0.8	...	26.9	0.3	0.21	0.34	[illegible]
3110	4.9	19.0	[illegible]	[illegible]	53.3	31.8	31.6	6.9	61.1	[illegible]	[illegible]	[illegible]	3.0	1.8	...	28.6	[illegible]	0.38	0.36	0.76
3140	[illegible]	[illegible]	[illegible]	[illegible]	61.3	39.9	[illegible]	8.0	130	[illegible]	65.9	103	2.1	3.1	[illegible]	30.3	0.4	0.55	[illegible]	0.70
3170	[illegible]	[illegible]	[illegible]	[illegible]	63.9	[illegible]	49.0	[illegible]	[illegible]	[illegible]	20.8	83.0	4.3	2.8	3.3	[illegible]	0.7	0.81	0.33	0.67
3200	21.8	[illegible]	[illegible]	[illegible]	72.9	[illegible]	[illegible]	9.3	1.3	13.8	9.1	49.0	6.9	4.3	...	[illegible]	0.9	1.3	0.31	0.63
3230	24.8	[illegible]	[illegible]	[illegible]	79.4	[illegible]	68.0	9.6	1.3	12.8	7.1	[illegible]	9.3	6.7	...	[illegible]	1.1	[illegible]	0.30	[illegible]
3260	[illegible]	[illegible]	82.8	15.1	81.3	[illegible]	78.0	11.1	1.3	12.8	6.2	31.0	13.1	9.2	...	[illegible]	1.3	[illegible]	0.28	0.60
3290	[illegible]	[illegible]	91.0	19.1	91.2	[illegible]	89.8	13.0	1.4	12.5	5.8	[illegible]	17.5	13.3	...	16.6	1.6	3.6	0.27	0.56
3320	[illegible]	[illegible]	101.0	21.4	91.9	[illegible]	92.1	16.3	2.0	13.6	5.9	[illegible]	[illegible]	17.9	...	14.0	1.8	[illegible]	0.26	0.55
3350	51.3	[illegible]	92.3	21.4	81.5	[illegible]	108	22.3	[illegible]	[illegible]	15.9	46.3	27.8	21.0	0.08	11.8	2.1	[illegible]	[illegible]	[illegible]
3380	56.7	[illegible]	94.3	[illegible]	92.7	[illegible]	[illegible]	[illegible]	2.2	13.0	[illegible]	[illegible]	31.4	27.6	...	10.0	2.3	[illegible]	0.21	[illegible]
3410	61.3	103	[illegible]	[illegible]	103	91.7	[illegible]	[illegible]	2.2	[illegible]	4.3	[illegible]	35.3	31.0	...	8.5	2.7	0.6	0.22	0.17
3440	65.9	101	[illegible]	[illegible]	101	93.8	[illegible]	21.6	1.8	[illegible]	4.1	[illegible]	39.2	31.8	...	6.8	3.0	2.5	[illegible]	0.16
3470	[illegible]	107	[illegible]	[illegible]	[illegible]	99.7	[illegible]	[illegible]	1.8	9.0	4.0	21.4	42.3	[illegible]	...	[illegible]	3.4	8.9	0.21	[illegible]
3500	[illegible]	117	139	[illegible]	[illegible]	105	153	[illegible]	1.9	[illegible]	3.5	[illegible]	43.1	39.7	0.14	[illegible]	3.9	10.3	0.20	[illegible]
3530	81.9	129	[illegible]	41.3	[illegible]	[illegible]	172	314	2.7	9.0	[illegible]	[illegible]	42.3	39.9	0.28	[illegible]	4.2	11.3	0.20	0.12
3560	[illegible]	[illegible]	[illegible]	[illegible]	130	[illegible]	138	[illegible]	3.0	[illegible]	3.2	[illegible]	41.8	38.6	0.42	[illegible]	[illegible]	[illegible]	0.19	0.40
3590	[illegible]	[illegible]	[illegible]	[illegible]	132	110	137	[illegible]	2.9	[illegible]	3.3	[illegible]	38.6	35.9	0.42	[illegible]	5.1	11.9	0.18	0.39
3620	92.9	[illegible]	[illegible]	[illegible]	130	126	185	255	3.0	11.6	4.1	[illegible]	[illegible]	31.8	0.49	[illegible]	5.5	15.8	0.18	0.38
3650	106	160	180	[illegible]	[illegible]	[illegible]	189	[illegible]	[illegible]	233	133	197	35.8	[illegible]	1.3	3.9	6.0	16.8	0.17	0.37
3680	118	170	194	[illegible]	[illegible]	[illegible]	230	[illegible]	608	331	188	221	27.8	26.3	1.9	[illegible]	6.4	18.3	0.17	0.36
3710	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	238	[illegible]	4.1	15.5	13.7	[illegible]	22.9	21.5	0.82	1.3	6.9	19.4	0.16	0.35
3740	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	232	[illegible]	3.4	[illegible]	1.6	95.1	19.1	17.7	0.96	1.3	7.8	20.4	0.16	0.33
3770	[illegible]	141	218	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	3.9	6.8	[illegible]	74.3	13.6	14.4	1.10	1.1	8.0	21.8	0.15	0.33
3800	[illegible]	193	210	41.0	169	[illegible]	308	[illegible]	4.3	7.9	4.3	100	12.7	11.4	[illegible]	1.1	8.4	22.5	0.16	0.33
3830	[illegible]	150	[illegible]	30.3	[illegible]	150	310	[illegible]	3.9	8.0	4.2	66.5	9.8	9.4	[illegible]	0.6	9.3	27.6	0.15	0.32
3860	120	[illegible]	196	[illegible]	[illegible]	161	294	3150	3.9	5.1	4.1	68.2	3.7	6.9	1.65	0.6	10.2	22.0	0.13	0.33
3890	[illegible]	198	[illegible]	[illegible]	140	161	305	4316	8.0	12.0	4.3	69.6	3.9	5.0	1.93	0.5	10.7	20.6	0.11	0.30
3920	133	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	300	142	2.1	16.1	4.9	[illegible]	4.9	3.9	[illegible]	0.5	11.3	19.2	0.13	0.28
3950	116	164	201	85.0	191	[illegible]	366	85.0	4.1	4.1	3.9	68.9	3.7	[illegible]	2.48	0.5	11.9	14.9	0.13	0.27
3980	[illegible]	[illegible]	265	113	198	101	400	16.0	5.4	3.3	3.8	69.2	2.8	1.9	2.60	0.5	12.8	13.6	0.13	0.28
4010	[illegible]	[illegible]	[illegible]	160	193	[illegible]	306	71.2	5.1	5.1	4.1	290	2.3	1.4	[illegible]	0.5	13.2	12.2	0.13	0.27
4040	[illegible]	[illegible]	[illegible]	166	188	[illegible]	301	91.4	68.8	202	37.8	303	9.8	3.7	14.1	6.4	13.8	8.7	0.11	0.26
4070	[illegible]	[illegible]	[illegible]	160	[illegible]	[illegible]	330	200	48.1	223	83.2	416	5.8	2.9	...	5.8	14.5	6.1	0.12	0.28
4100	336	310	386	[illegible]	198	[illegible]	363	363	12.4	49.3	16.5	213	1.6	0.5	4.17	0.5	13.4	4.5	0.11	0.18

*GE Sunlamp

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<u>Outdoor Tests</u>: A sterile 100 ml of ring-^{14}C FMC 57020 (20 uCi, 100 ppm) solution (water, pH 5.8) in a sterilized flask was placed under direct sunlight for 30 days. A dark control flask was wrapped with aluminum foil. Aliquots (3 ml) were removed from irradiation flasks on days 0, 14 and 30. A dark control sample was taken at the 30 day interval.

The samples were processed by passing the water through an activated C-18 Sep-Pak® column followed by elution with CH_2Cl_2. The organic fraction was concentrated and assayed by HPLC.

<u>Indoor Tests</u>: Test concentrations of 1 or 100 ppm of methylene-^{14}C FMC 57020 were prepared in volumes of 100 ml of water and about 10 uCi of radioactivity. Acetone was added to certain test solutions at 0.1 or 2.0 %. Irradiation was continuous. A number of tests were run to provide the necessary data and the tests are summarized below:

SUMMARY OF INDOOR PHOTOLYSIS CONDITIONS

Test No.	FMC 57020 Concentration (ppm)	Acetone Concentration (%)	Sampling Intervals (Days)
1	1 1/	0	0,1,3,7,14
2	1 1/	0	0,7,14
3	1 1/	2	0,7
4	1	2	0,1/3,1/2,1,2,3,4,5,7
5	1	0.1	0,1/3,1/2,1,2,3,4,5,7
6	100	0	0,1,3,7,14
7	100	2	0,28
8	100 2/	2	0,28

1/ Non-irradiated (dark control) samples

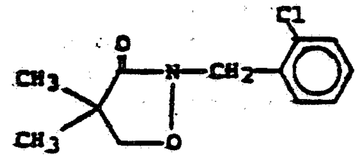
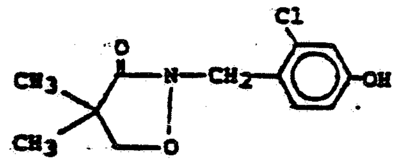
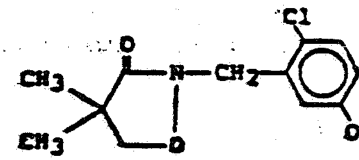
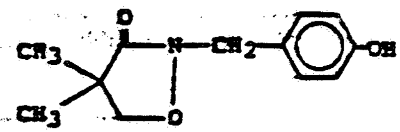
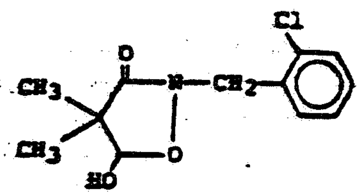
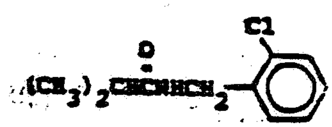
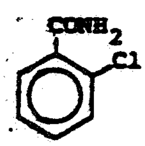
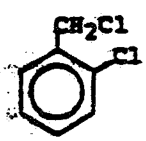
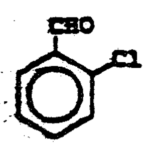
2/ All solutions were prepared using methylene-^{14}C FMC 57020 except for test solution No. 8 which contained only non-labeled chemical.

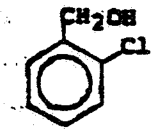
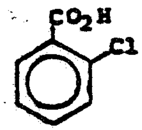
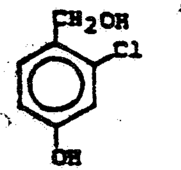
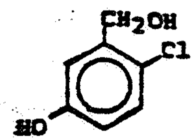
Most of the samples were assayed directly by HPLC. Samples from day 28 of tests 7 and 8 were subjected to ethylacetate partitioning and then HPLC and GC/MS analyses.

Polar metabolites were derivatized (trimethylsilylation with N,O-bis-(trimethylsilyl)-trifluoroacetamide; methylation with diazomethane) and subjected to GC/MS analysis.

Radioactivity in the various extracts and HPLC fractions was determined by LSC.

The following standard compounds were used for the identification of degradation products.

	FMC Number	Name	Structure
A)	FMC 57020	2-[(2'-Chlorophenyl)methyl]-4,4-dimethyl-3-isoxazolidinone	
B)	FMC 62667	2-[(2'-Chloro-4'-hydroxyphenyl)methyl]-4,4-dimethyl-3-isoxazolidinone	
C)	FMC 77039	2-[(2'-Chloro-5'-hydroxyphenyl)methyl]-4,4-dimethyl-3-isoxazolidinone	
D)	FMC 62632	2-[(4'-Hydroxyphenyl)-methyl)]-4,4-dimethyl-3-isoxozolidinone	
E)	FMC 60217	2-[(2'-Chlorophenyl)-methyl]-4,4-dimethyl-5-hydroxy-3-isoxazolidinone	
F)	FMC 55657	N-[(2'-Chlorophenyl)methyl]-2-methyl propanamide	
G)	FMC 3133	2-Chlorobenzamide	
H)	FMC 3436	2-Chlorobenzyl chloride	
I)	FMC 14788	2-Chlorobenzaldehyde	

FMC Number	Name	Structure
J) FMC 61569	2-Chlorobenzyl alcohol	
K) FMC 14791	2-Chlorobenzoic acid	
L) FMC 87015	2-Chloro-4-hydroxybenzyl alcohol	
M) FMC 87016	2-Chloro-5-hydroxybenzyl alcohol	

Results

FMC 57020 remaining in aqueous solution following the exposure to natural (outdoor tests) or simulated (indoor tests) sunlight is summarized in the following table.

SUMMARY OF FMC 57020 REMAINING IN AQUEOUS SOLUTION FOLLOWING EXPOSURE TO NATURAL AND ARTIFICIAL SUNLIGHT[1/]

Time (Days)	% FMC 57020							
	Outdoor Tests		Indoor Tests					
	Irradiated	Control	#1	#4	#5	#6	#2 (Control)	#3 (Control)
0	99.3	99.3	95.1	98.5	98.5	95.3	95.1	98.6
1/3	-	-	-	79.0	88.9	-	-	-
1/2	-	-	-	63.8	87.9	-	-	-
1	-	-	93.8	36.9	82.7	95.5	-	-
2	-	-	-	13.7	66.7	-	-	-
3	-	-	92.9	6.8	53.6	93.3	-	-
4	-	-	-	2.7	43.9	-	-	-
5	-	-	-	1.9	36.6	-	-	-
7	-	-	88.0	1.2	29.4	90.4	98.0	96.6
14	86.1	-	81.1	-	-	83.3	98.6	-
28	-	-	-	-	-	-	-	-
30	78.1	94.8	-	-	-	-	-	-

[1/] Data derived by HPLC assay of either methylene chloride or aqueous fractions obtained from various tests for FMC 57020.

The half-life of FMC 57020 in various conditions is summarized below.

	Ring-^{14}C Outdoor Test	Methylene-^{14}C Indoor Tests			
Test #	-	#6	#1	#4	#5
FMC 57020 conc. (ppm)	100	100	1	1	1
Acetone conc. (%)	0	0	0	2.0	0.1
t 1/2 reported (day)	67.5	47.5	NR	0.77	3.51
t 1/2 EAB calculated	87.1	70.2	60.6	1	3.8

The rate of FMC 57020 decomposition in all dark control solutions was negligible.

The HPLC analyses of the 28 day samples containing 100 ppm FMC 57020 indicated the presence of at least 7 major components and at least 20 minor components (figure 1). A total of 87.2 % of the photo-products could be partitioned in ethyl acetate. An HPLC analysis of this EtOAc extract indicated that all the the major photoproducts were organoextractable.

The GC/MS analysis showed the presence of 2-chlorobenzaldehyde 2-chlorobenzyl alcohol, 2-chlorobenzoic acid and 2-chlorobenzamide as well as parent compound, FMC 57020. Some minor products were identified after derivatization. These were hydroxy pivalic acid and a substituted imide, 4,4-dimethyl-3-isoxazolidinone (heterocyclic fragment of FMC 57020), 2-chloroacetophenol, 2-chloromethylbenzoate and FMC 57019, a rearrangement product of FMC 57020. The distribution of the photoproducts detected is shown in the following tables.

Data indicated that the breakdown of FMC 57020 is accompanied by the formation of 2-chlorobenzoic acid (FMC 14791) which was a major photodegradate. Two polar, volatile fractions appeared to build up with time. It was assumed that these fractions resulted from extended decomposition of 2-chlorobenzoic acid.

The proposed photochemical degradation pathway for FMC 57020 in water is shown in figure 1.

Comments/Questions

- The half-life estimations reported are different from those calculated by the reviewer. The photodecomposition rate in water under sunlight was estimated by a plot of percent FMC 57020 remaining vs time (see Figure 2, appended), while that in water containing acetone under simulated sunlight was estimated by a plot of log concentration vs. time (fig. 3, appended).

FIGURE 1

PROPOSED PHOTOCHEMICAL DEGRADATION PATHWAY FOR FMC 57020 IN WATER

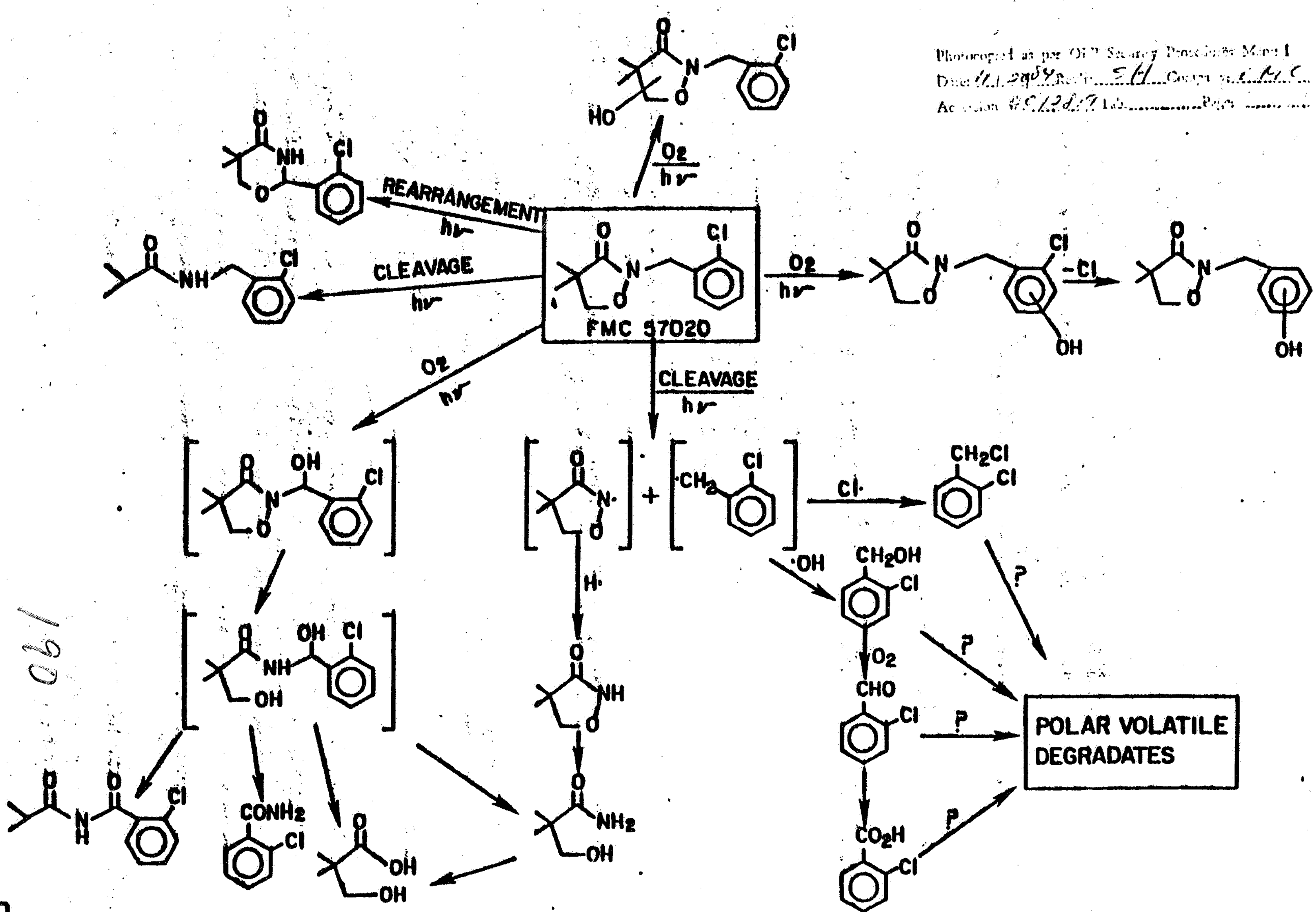


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TABLE

DISTRIBUTION OF PRODUCTS DETECTED IN SUNLAMP IRRADIATED SOLUTIONS CONTAINING 1 PPM FMC 57020 AND 2% ACETONE

Fractions	0-Day	1/3-Day	1/2-Day	1-Day	2-Day	3-Day	4-Day	5-Day
FMC 14791		3.0	5.9	12.9	18.8	21.6	22.8	26.8
Fraction A 1/		1.7	4.3	10.4	16.9	19.2	22.0	20.7
Fraction B 2/		1.7	4.4	9.9	15.9	20.5	22.5	22.7
FMC 3133		0.5	0.8	1.4	1.8	1.7	1.6	1.7
FMC 87015		0.4	1.0	1.9	3.0	3.1	3.3	2.9
FMC 87016		0.5	1.1	3.2	3.0	3.0	3.4	2.2
FMC 62632		0.6	1.0	1.3	1.8	1.7	1.6	1.7
FMC 61569		0.4	0.8	1.0	1.1	1.2	1.0	0.9
FMC 62667		0.3	0.6	0.7	0.6	0.3	0.3	0.8
FMC 60217		0.5	0.9	0.9	0.8	0.6	0.6	0.5
Arylimide		0.9	1.2	1.5	1.4	0.7	0.6	0.3
FMC 55657		0.9	1.5	2.0	1.3	1.1	0.9	1.2
FMC 14788		1.5	1.5	1.4	1.4	0.8	0.6	0.5
FMC 57020	98.5	79.0	63.8	36.9	13.7	6.8	2.7	1.9
FMC 3436		2.6	1.5	1.4	1.2	0.7	0.9	0.8
Unknowns 3/		6.5	9.7	13.2	17.3	17.0	15.2	14.4

1/ HPLC R_t = 4-6 minutes
2/ HPLC R_t = 6-8 minutes
3/ Includes at least 7 unknowns, none exceeding 4.0%

TABLE

DISTRIBUTION OF PRODUCTS DETECTED IN SUNLAMP IRRADIATED SOLUTIONS CONTAINING 1 PPM FMC 57020 AND 0.1% ACETONE

Fractions	0-Day	1/3-Day	1/2-Day	1-Day	2-Day	3-Day	4-Day	5-Day
FMC 14791		1.2	1.9	3.7	8.3	11.7	16.1	19.5
Fraction A 1/		0.4	0.6	2.1	7.0	12.0	16.2	23.4
Fraction B 2/		0.3	0.5	1.2	3.4	6.9	8.0	6.7
FMC 3133		0.3	0.4	0.6	1.2	1.5	1.6	1.8
FMC 87015		0.2	0.2	0.3	0.5	0.8	0.8	0.8
FMC 87016		0.3	0.4	0.5	0.7	0.9	0.8	0.6
FMC 62632		0.5	0.5	0.7	1.0	0.9	0.7	0.6
FMC 61569		0.3	0.2	0.3	0.5	0.7	0.7	0.7
FMC 62667		0.2	0.2	0.2	0.3	0.3	0.3	0.4
FMC 60217		0.3	0.3	0.3	0.5	0.4	0.4	0.4
Arylimide		0.5	0.5	0.5	0.7	0.6	0.6	0.6
FMC 55657		0.4	0.4	0.4	0.4	0.5	0.5	0.4
FMC 14788		1.4	1.4	2.0	3.1	3.3	3.1	3.0
FMC 57020	98.5	88.9	87.9	82.7	66.7	53.6	43.9	36.6
FMC 3436		1.1	1.5	1.4	0.8	0.9	0.7	0.7
Unknowns 3/		3.7	3.1	3.1	4.9	5.0	5.6	3.8

1/ HPLC R_t = 4-6 minutes
2/ HPLC R_t = 6-8 minutes
3/ Also includes at least 7 unknowns, none exceeding 1.0%

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FIGURE 2

PHOTODECOMPOSITION OF FMC 57020 IN WATER EXPOSED TO NATURAL AND ARTIFICIAL LIGHT

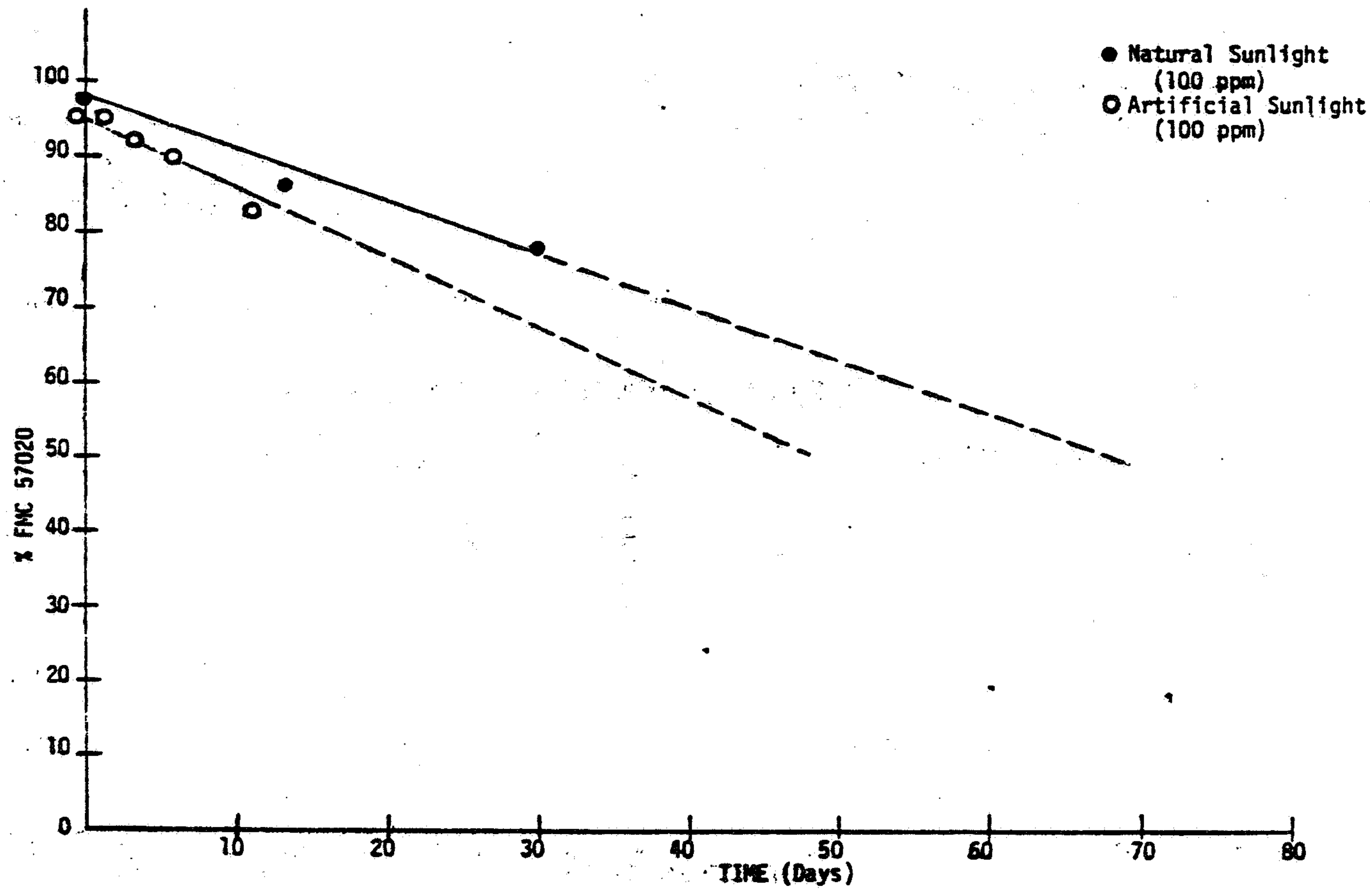

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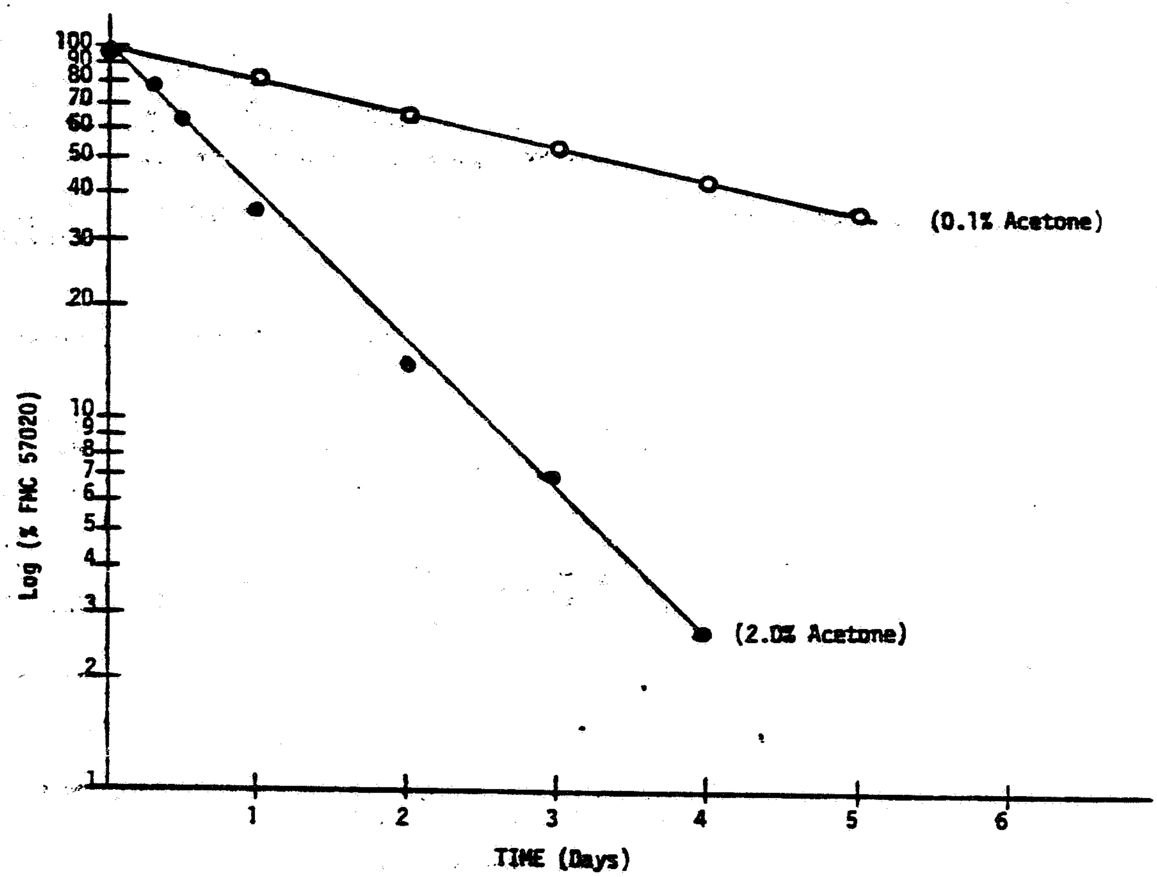
FIGURE 3

PHOTODECOMPOSITION RATE OF FMC 57020 IN WATER CONTAINING ACETONE



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Why wasn't log concentration vs. time used to estimate the half-lives in both sensitized and nonsensitized experiments?

- No description about the temperature of the photolysis solutions.
- No organic volatile traps were installed.
- Actual recovery rates were not reported - only normalized % distribution of radio residue was reported.

Conclusion

FMC 57020 appears to undergo photodecomposition to give 2-chlorobenzoic acid (a major product) and many other degradates with a half-life about 87 days (67.5 days was reported) under natural sunlight.

Breakdown of FMC 57020 under the irradiation with a GE sunlamp was similar to that observed under sunlight. Acetone facilitated degradation, and the degradation rate increased with increasing concentration of acetone relative to FMC 57020.

This study is not accepted for the following reasons:

1) Half-lives were not derived in a consistent manner.

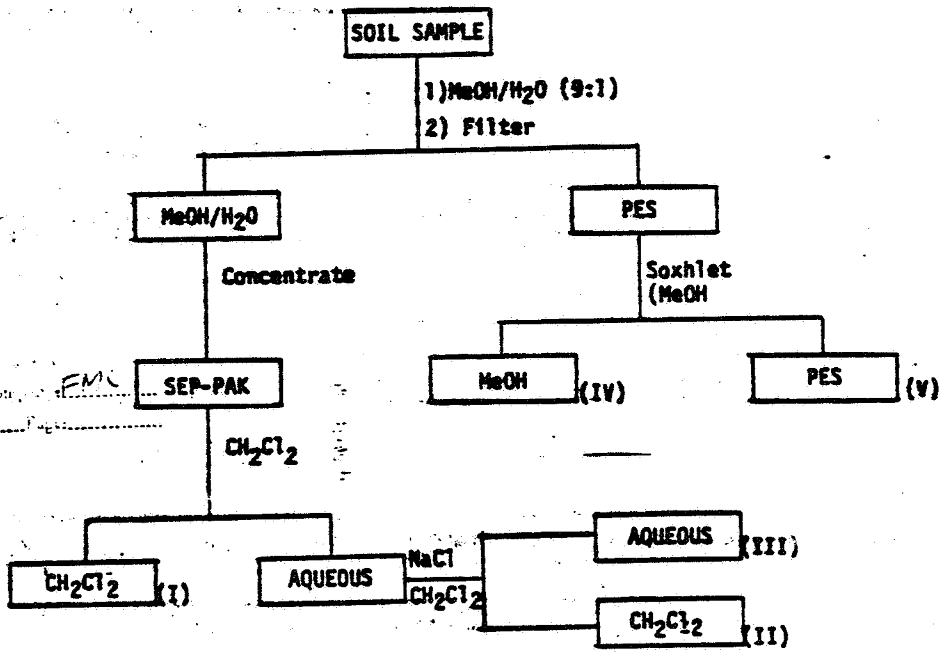
2) Actual recoveries of radioactivity (loss due to non-trapped volatiles) were not reported.

3.2 Photodegradation of FMC 57020 in/on Soil. J. Wu, FMC Corp. P-0873, 5/11/84, Notebook Rf. E3014, E 2743, EPA Acc. No. 072819 (Rf. 3).

Experimental

Dunkirk silt loam soil (20g, dried, sieved) was mixed with distilled water (20 ml) in a petri plate (15 cm i.d.). The soil plate was allowed to dry overnight yielding a thickness of about 0.25 cm. Each plate was evenly treated with ring-^{14}C-FMC 57020 (5.9 mg, 2.5 uCi/plate) equivalent to a rate of 3 lb ai/a. Four treated soil plates were covered with Mylar film and irradiated directly with natural sunlight. One control plate was wrapped with aluminum foil. Soil samples were removed for analysis on days 0, 14 and 30.

Soil samples were extracted according to the following scheme.



Aliquots of each fractions (I, II, IV) of each sample were diluted with cold FMC 57020 and analyzed by HPLC. Radioactivity in the various extracts and HPLC fractions was determined by LSC. Post extraction solids were assayed by combustion/LSC.

Results

The following table shows the recovery of ^{14}C residues.

RECOVERY OF FMC 57020 AND DEGRADATES FROM SOIL EXPOSED TO SUNLIGHT

	% ^{14}C Distribution			
Fractions[1/]	0 Day	14 Day	30 Day	30 Day Control
Methylene Chloride (I + II)[2/]	95.8	91.4	81.8	94.0
FMC 57020	(95.6)[3/]	(85.2)	(75.1)	(91.4)
Polar Degradates	(0.1)	(3.7)	(3.3)	(1.4)
Non-Polar Degradates	(0.1)	(2.5)	(3.4)	(1.2)
Methanol (IV)	[4/]	[4/]	5.0	4.8[5/]
FMC 57020			(3.2)	(N/A)
Polar Degradates			(1.7)	(N/A)
Non-Polar Degradates			(0.1)	(N/A)
Aqueous (III)	0.7	1.6	4.9	0.1
Non-Extractable (V)	3.5	7.0	8.3	1.1
Total	100.0	100.0	100.0	100.0
% Recovery of Applied ^{14}C	92.7	74.4	71.0	87.0

Material balance was 74.4 % for 14 day sample, 71 % for the 30 day sample and 87.0 % for the 30 day control.

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Conclusion/Recommendation

This study can not be accepted for the following reasons:

1) Volatile compounds were not trapped; so, material balance was poor.

2) Soil was not sterilized; microbial metabolism is expected. The results from the 30 day control analysis indicate that degradation of FMC 57020 occurred through mechanisms other than photolysis.

3) The temperature of soil was not mentioned.

4) Degradation rate was neither reported nor can be estimated. Microbial degradation might have been involved.

5) Identification of degradation products was not done.

6) The Mylar film may have excluded those wavelenths that could cause photodegradation.

3.3 Degradation of FMC 57020 ^{14}C-Methylene in Clay Loam, Silt Loam and Sandy Loam Soil under Aerobic Conditions. L.W. Froelich, M-4860, June 7, 1982, Rf. E1536, E1838. EPA Acc. No. 072819 (Rf. 4).

This report was previously reviewed (EAB review dated Dec. 2, 1982). It was concluded that the half-life of ^{14}C - methylene FMC 57020 is more than 56 days (last sampling day) in a silt loam and a clay loam and is about 28 days in a sandy loam soil. Degradation to CO_2 and soil binding appeared to be the primary route of dissipation.

Appendix C of the present submission (appended) contains the addendum data from the 112 day sample analysis.

Comments

The reported half-lives of FMC 57020 in the soils studied are different from those obtained by the reviewer. From the linear regression, the half-lives of 43.9 days in Cosad sandy loam, 95.4 days in Hagerstown clay loam and 104.3 days in Dunkirk silt loam were obtained using six data points including the new data from 112 day analysis.

It is noted that volatile organic compounds were not monitored (only CO_2 was monitored) and the recoveries were reported as a range (75.3 102.3%). Since it is not known whether the loss (-2.3 24.7%) was due to volatiles or extraction procedures, the half-life estimations from the normalized % values are not considered to be right.

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APPENDIX C

Table 5 gives the 112 day material balance profile for the degradation of FMC 57020 in Cosad sandy loam, Dunkirk silt loam and Hagerstown clay loam soils. The half-life of FMC 57020 is approximately 99 days in both Dunkirk silt loam and Hagerstown clay loam. The half-life of FMC 57020 was found to be approximately 28 days in Cosad sandy loam.

Minor levels (<1.0% total) of unidentified metabolites were found in the soil extracts. $^{14}CO_2$ evolution increased to 43.5% in the Cosad sandy loam while in the Dunkirk silt loam and Hagerstown clay loam soils $^{14}CO_2$ evolution was 8.3% and 19.6%, respectively. At 112 days post extraction solids (PES) had increased to 39.3% in the Cosad sandy loam, 50.5% in the Dunkirk silt loam and 40.9% in the Hagerstown clay loam.

TABLE 5

Methylene ^{14}C FMC 57020
112 day Material Balance 1)

PRODUCT	COSAD SANDY LOAM	DUNKIRK SILT LOAM	HAGERSTOWN CLAY LOAM
FMC 57020	16.1	40.4	38.5
Unidentified Products	0.8	0.7	0.9
Total Nonpolar	16.9	41.1	39.4
Polar	0.3	0.1	0.1
$^{14}CO_2$	43.5	8.3	19.6
PES	39.3	50.5	40.9
Total	100.0	100.0	100.0

1) Represents a normalized % distribution of total recovered ^{14}C. Recoveries based on applied radiocarbon ranged from 75.3% to 102.3%.

Conclusion

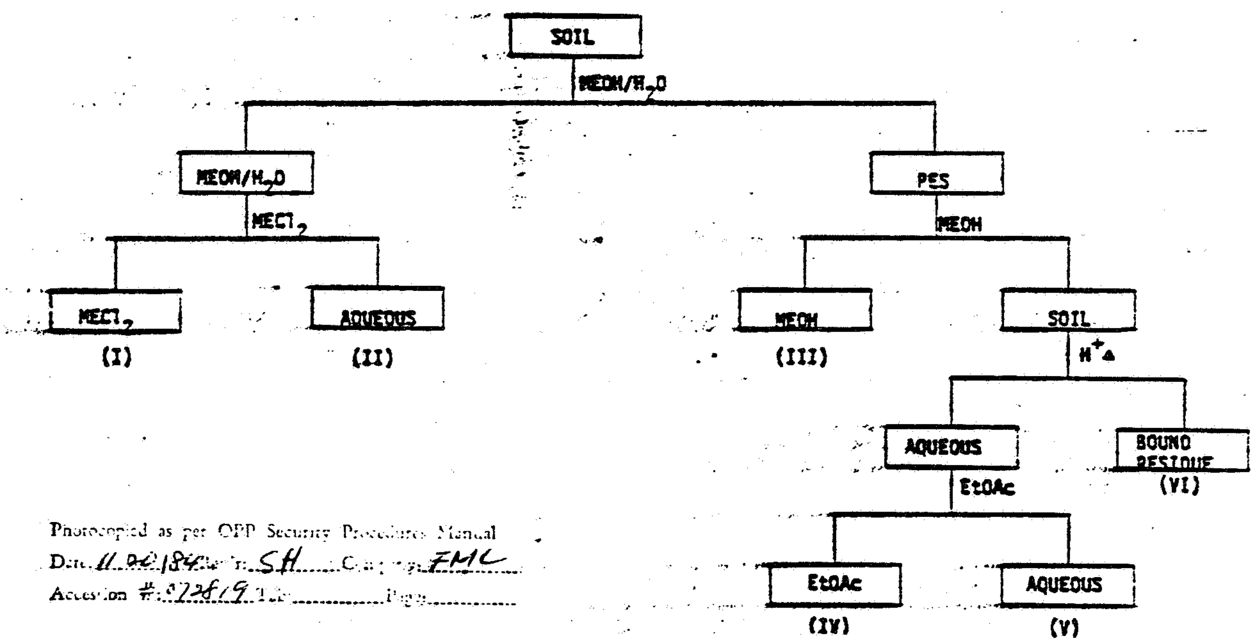
The same conclusion from the previous review (12/2/84) stands except the half-life estimations (see "Comments").

This study is not acceptable for the aerobic soil metabolism data requirement until the points in the "Comments" section above are addressed.

3.4 Analysis of FMC 57020 Soil Bound Residues. T. A. Bixler, FMC Corp. P-0878, 5/21/84, Rf. E1855, E2382, EPA Acc. No. 072819 (Rf. 5).

Experimental

Non-extractable residues remaining in sandy loam and clay loam soils after 28, 56 and 112 days (section 3.3, above) were subjected to Soxhlet extraction with methanol followed by acid (HCl) hydrolysis. The methanol extract was analyzed by TLC/autoradiography. The hydrolysis solution was partitioned in EtOAc and the EtOAc fraction was subjected to HPLC/TLC analyses. The extraction scheme is shown below.



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Radioassay was done on liquid and solid samples and the individual radioactive spots on TLC plates.

Results

The previous study (section 3.3) showed that most of the radioactivity recovered in Methanol/H_2O was attributed to unaltered FMC 57020. The continuous extraction of the non-extractable soil residues with methanol released additional unaltered FMC 57020 (4.4-10.2%). Acid hydrolysis also resulted in removal of ^{14}C residues. Unaltered FMC 57020 comprised a significant portion (75-90%) of the radioactivity. The results are summarized in the tables 1 and 2.

Conclusion

About 40% of the non-extractable residues after methanol/H_2O blending could be released by soxhlet extraction and acid digestion. Parent compound, FMC 57020 comprised 75-90% of the released residues.

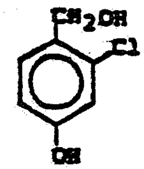
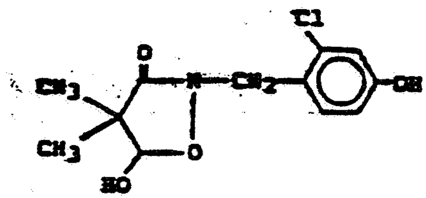
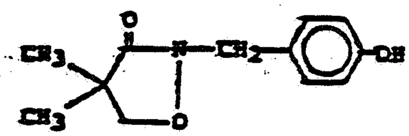
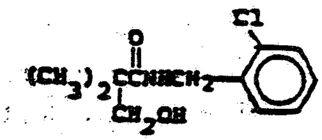
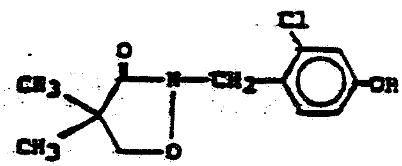
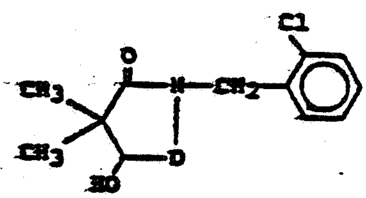
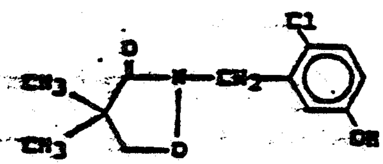
Recommendation

Since the position of labeling was in methylene moiety of the compound, it can be expected that parent compound and $^{14}CO_2$ would comprise significant portions of the radioactivity recovered. Soil metabolism studies (this study and the study in section 3.3) with methylene-^{14}C FMC 57020 can tell the decomposition rate of the compound. However, a study using ring-^{14}C FMC 57020 would be beneficial in determining the soil metabolites of the compound.

3.5 Metabolism of Carbonyl-^{14}C and Ring-^{14}C FMC 57020 in Soil under Aerobic and Anaerobic Conditions. T.A. Bixler, FMC Corp. P-0881, 5/24/84, Notebook Rf. E2885, E3443, EPA. Acc. No. 072819 (Rf 6).

Using carbonyl-^{14}C 57020 (20.04 mCi/mM, 98.4% pure and ring-^{14}C 57020 (20.12 mCi/mM, 97.8% pure), soil metabolism study of FMC 57020 was done to provide additional soil degradation information.

For the identification of metabolites, reference compounds were used in HPLC; they are listed on the following pages.

	FMC Number	Name	Structure
A)	FMC 87015	2-Chloro-4-hydroxybenzyl alcohol	
B)	FMC 83918	2-[(2'-Chloro-4'-hydroxyphenyl)-methyl]-5-hydroxy-4,4-dimethyl-3-isoxazolidinone	
C)	FMC 62632	2-[(4'-Hydroxyphenyl)-methyl)]-4,4-dimethyl-3-isoxozolidinone	
D)	FMC 65317	N-[(2'-Chlorophenyl)methyl]-3-hydroxy-2,2-dimethyl propanamide	
E)	FMC 62667	2-[(2'-Chloro-4'-hydroxy-phenyl)methyl]-4,4-dimethyl-3-isoxazolidinone	
F)	FMC 60217	2-[(2'-Chlorophenyl)-methyl]-4,4-dimethyl-5-hydroxy-3-isoxazol-idinone	
G)	FMC 77039	2-[(2'-Chloro-5'-hydroxy-phenyl)methyl]-4,4-dimethyl-3-isoxazolidinone	

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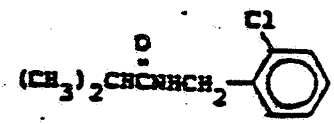
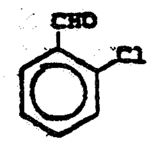
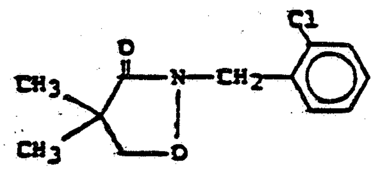
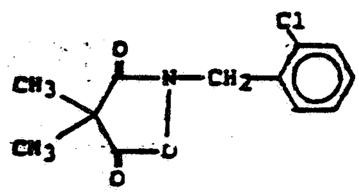
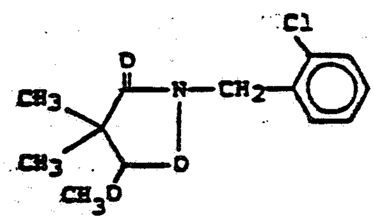
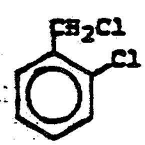
	FMC Number	Name	Structure
H)	FMC 55657	N-[(2'-Chlorophenyl)methyl]-2-methyl propanamide	
I)	FMC 14788	2-Chlorobenzaldehyde	
J)	FMC 57020	2-[(2'-Chlorophenyl)methyl]-4,4-dimethyl-3-isoxazolidinone	
K)	FMC 55626	2-[(2'-Chlorophenyl)methyl]-4,4-dimethyl-5-oxo-3-isoxazolidinone	
L)	FMC 57061	2-[(2'-Chlorophenyl)-methyl]-4,4-dimethyl-5-methoxy-3-isoxazolidinone	
M)	FMC 3436	2-Chlorobenzyl chloride	

Three soil types were used and their properties are summarized in table 1.

Table 1

Soil	Texture - % Sand	Silt	Clay	Organic Matter (%)	CEC[1]	pH	Bulk Density[2]
Hagerstown Silty Clay Loam[3]	20.8	54.8	24.0	2.3	13.8	7.5	1.16
Dunkirk Silt Loam	30.4	55.2	14.4	3.1	14.2	7.1	1.13
Cosad Sandy Loam	54.4	35.2	10.4	3.0	16.1	7.0	1.18

1/ Cation exchange capacity expressed as meq/100 g.

2/ Expressed as g/cm^3.

3/ Soil textural analysis data indicate that the particular sample used in this study was generically classified as a "silt loam" soil; however, the classification "silty clay loam" has been retained due to the soil's higher clay content and a desire to be consistent with prior literature classification (81).

Soil treatment is summarized in table 2.

Table 2

Soil type (50 g Dry Wt.)	Aerobic	Anaerobic	Labeling Position	Radioact.	Conc.
Cosad Sandy loam	X	X	Carbonyl	10.23 uCi	2.45 ppm
Dunkirk silt loam	X	X	Ring	9.33 uCi	2.22 ppm
Hagerstown clay loam	X		Carbonyl	10.23 uCi	2.45 ppm
	X		Ring	9.33 uCi	2.22 ppm

All tests were incubated at 25 ± 3°C in the absence of light. Duplicate soil samples were taken at 0 time, 2, 4, 6 and 9 months from treatment. Control samples were taken at 0 time and 9 months.

Anaerobic tests were done after aging the treated soils for 60 days prior to flooding with water. Dried alfalfa hay was mixed into each sample.

Evolving CO_2 was trapped in a KOH solution.

The soil extraction procedure was the same as described in sections 3.3 and 3.4.

Water layers from the anaerobic tests were decanted from the soil, filtered and passed through Sep-Pak. The Sep-pak was eluted with CH_2Cl_2.

HPLC, TLC, GC/MS and LSC were used for quantitation and/or identification of products.

Results

The results obtained from the carbonyl-^{14}C FMC 57020 aerobic test on Cosad sandy loam are summarized in table 3.

Table 3

	0 Time		2 Month		4 Month		6 Month		9 Month	
	% Dist.	% FMC 57020	% Dist.	% FMC 57020	% Dist.	% FMC 57020	% Dist.	% FMC 57020	% Dist.	% FMC 57020
$MeCl_2$ (I)	96.6	95.4	32.3	31.0	15.3	14.1	7.0	6.4	6.5	5.9
MeOH (III)			3.8	3.3	3.2	2.5	2.0	1.6	1.2	1.0
EtOAc (IV)			2.4	1.1	3.5	1.8	2.6	1.2	3.0	1.5
Total FMC 57020		95.4		35.4		18.4		9.2		8.4
Unidentified Products 2/	1.2		3.1		3.6		2.4		2.3	
Total Organosolubles	96.6		38.5		22.0		11.6		10.7	
Polar Aqueous (II, V)			3.1		3.1		3.1		3.2	
$^{14}CO_2$			49.0		62.7		73.6		76.9	
Bound Residues (VI)	3.4		9.4		12.2		11.7		9.2	
TOTAL	100.0		100.0		100.0		100.0		100.0	

1/ Normalized percent distribution of total recovered ^{14}C. Recoveries based on 0 day data ranged from 86.6%-91. Residue levels (µg/g) of FMC 57020 may be found in Appendix J.

2/ Unidentified metabolites (7), none exceeding 0.9%. Percentage is total from organic fractions I, III, IV.

The recoveries based on 0 day data ranged 86.6% - 91.7%.

As the level of FMC 57020 decreased with time (95.4% at 0 time to 8.4% at 9 months), the evolved CO_2 increased (76.9% at 9 months). An estimated half-life of 36 days was reported. The reviewer estimated a half-life to be 55.5 days.

The results obtained from the ring ^{14}C FMC 57020 aerobic test in Dunkirk silt loam and carbonyl- and ring ^{14}C FMC 57020 aerobic test in Hagerstown silty loam are in tables 4 and 5.

In silt loam, ring ^{14}C FMC 57020 degraded at a steady but slower rate. The calculated half-life of 137 days (173.1 day by the reviewer) was reported.

Degradation of ring-^{14}C FMC 57020 and carbonyl-^{14}C FMC 57020 was very similar in Hagerstown silty loam soil. Half-lives could not be obtained due to lack of data points. At 9 months, less than 1% of parent compound was detected.

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TABLE 4

RING-^{14}C FMC 57020 - AEROBIC TEST
DUNKIRK SILT LOAM SOIL
MATERIAL BALANCE[1]/PRODUCT DISTRIBUTION

	0 Day		2 Month		4 Month		6 Month		9 Month	
	% Dist.	% FMC 57020	% Dist.	% FMC 57020	% Dist.	% FMC 57020	% Dist.	% FMC 57020	% Dist.	% FMC 57020
$MeCl_2$ (I)	95.5	94.8	54.0	53.1	36.2	34.4	29.5	28.7	20.4	19.7
MeOH (III)			6.1	6.0	7.8	7.3	7.9	7.3	5.5	4.5
EtOAc (IV)			4.4	3.8	6.9	6.1	6.6	5.8	7.4	6.4
Total FMC 57020		94.8		62.9		47.8		41.8		30.6
Unidentified Products[2]	0.7		1.6		3.1		2.2		2.7	
Total Organosolubles	95.5		64.5		50.9		44.0		33.3	
Polar Aqueous (II,V)	0.6		2.2		2.4		3.6		2.7	
$^{14}CO_2$			22.1		31.5		35.4		47.8	
Bound Residues (VI)	3.9		11.2		15.2		17.0		16.2	
TOTAL	100.0		100.0		100.0		100.0		100.0	

[1]/Normalized percent distribution of total recovered ^{14}C. Recoveries based on 0 day data ranged from 90.4-100.0%. Residue levels (µg/g) of FMC 57020 may be found in Appendix J.

[2]/Unidentified metabolites (7), none exceeding 0.5%. Percentage is total from organic fractions I, III, IV.

TABLE 5

CARBONYL-^{14}C AND RING-^{14}C FMC 57020 - AEROBIC TEST
HAGERSTOWN SILTY CLAY LOAM SOIL
MATERIAL BALANCE[1]/PRODUCT DISTRIBUTION

	Carbonyl-^{14}C FMC 57020				Ring-^{14}C FMC 57020			
	6 Month		9 Month		6 Month		9 Month	
	% Dist.	% FMC 57020	% Dist.	% FMC 57020	% Dist.	% FMC 57020	% Dist.	% FMC 57020
$MeCl_2$ (I)	1.8	1.5	1.0	0.8	1.6	1.4	1.1	1.0
MeOH (III)	1.1	0.8	N/A[2]		1.0	0.7	N/A	
EtOAc (IV)	3.2	1.8	N/A		2.2	1.5	N/A	
Total FMC 57020		4.1		0.8		3.6		1.0
Unidentified Products[3]	2.0		0.2		1.2		0.1	
Total Organosolubles	6.1		1.0		4.8		1.1	
Polar Aqueous (II, V)	3.0		0.1		3.4		0.2	
$^{14}CO_2$	76.8		78.8		66.9		68.1	
Bound Residues (VI)	14.1		20.1		24.9		30.6	
TOTAL	100.0		100.0		100.0		100.0	

[1]/Normalized percent distribution of total recovered ^{14}C. Recoveries based on 0 day data (Cosad and Dunkirk soils) and ranged from 87.6-100.6%.

[2]/Soils not subjected to MeOH soxhlet or acid hydrolysis.

[3]/Unidentified metabolites (5-7), none exceeding 0.4%. Six-month percentage is total from organic fractions I, III, and IV.

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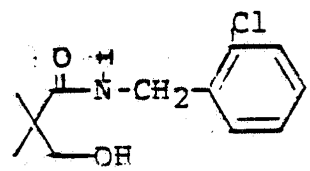
Comparison of $^{14}CO_2$ evolution from the three soil types (Figure 1) indicates that both the heterocyclic and aromatic moieties are equally susceptible to mineralization process and the degree of mineralization varied with soil type not with position of labeling.

Analysis of the extracts from anaerobic soil and water samples by TLC indicated the presence of one major and several minor metabolites. The major metabolite from both carbonyl- and ring-^{14}C labeled samples was identified as FMC 65317, the reductive N-O bond cleavage product of parent compound.



The distribution of the radioactivity is shown in tables 6 and 7.

The analyses indicated that the parent compound remaining after aerobic mineralization degrades to FMC 67317 under anaerobic conditions.

TABLE 6 CARBONYL-^{14}C FMC 57020 - ANAEROBIC TEST
COSAD SANDY LOAM SOIL

	30 Day			60 Day		
	% Dist.	% FMC 57020	% FMC 65317	% Dist.	% FMC 57020	% FMC 65317
Water Layer						
$MeCl_2$ (VII)	8.1	0.5	6.6	12.5	-	11.5
Polar Aqueous (VIII)	5.7			6.9		
Soil Layer						
$MeCl_2$ (I)	7.6	2.0	4.7	8.0	0.7	6.6
MeOH (III)	2.7	1.0	0.5	2.3	0.6	0.7
EtOAc (IV)	3.6	1.3	-	3.0	1.1	0.5
Total FMC 57020		4.8			2.4	
Total FMC 65317			11.8			19.3
Unidentified Products 2/	5.4			4.1		
Total Organosolubles 3/	22.0			25.8		
Polar Aqueous (VIII)	5.7			6.9		
Polar Aqueous (II, V)	6.3			6.0		
$^{14}CO_2$	55.5			51.0		
Bound Residues (VI)	10.5			10.3		
TOTAL	100.0			100.0		

1/ Normalized percent distribution of total recovered ^{14}C. Recoveries based on 0 day aerobic test ranged from 79.3-88.5%. Residue levels (µg/g) of FMC 57020 and FMC 65317 may be found in Appendix K.

2/ Unidentified metabolites (8), none exceeding 0.5%. Percentage is total from organic fractions I, III, IV, and VII.

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TABLE 7 RING-^{14}C FMC 57020 – ANAEROBIC TEST DUNKIRK SILT LOAM SOIL

	30 Day			60 Day		
	% Dist.	% FMC 57020	% FMC 65317	% Dist.	% FMC 57020	% FMC 65317
Water Layer						
$MeCl_2$ (VII)	24.0	7.6	14.3	27.4	0.7	25.0
Polar Aqueous (VIII)	4.6			7.6		
Soil Layer						
$MeCl_2$ (I)	18.8	9.6	8.1	13.3	1.7	10.5
MeOH (III)	4.8	3.1	0.8	4.9	2.2	1.4
EtOAc (IV)	6.8	4.5	-	5.1	3.6	1.0
Total FMC 57020		24.8			8.2	
Total FMC 65317			23.2			37.9
Unidentified Products[2/]	5.4			4.6		
Total Organosolubles[3/]	54.4			50.7		
Polar Aqueous (VIII)	4.6			7.6		
Polar Aqueous (II, V)	3.0			3.6		
$^{14}CO_2$	23.5			25.6		
Bound Residues (VI)	14.5			12.5		
TOTAL	100.0			100.0		

1/ Normalized percent distribution of total recovered ^{14}C. Recoveries based on 0 day aerobic test ranged from 94.8-98.6%. Residue levels (µg/g) of FMC 57020 and FMC 65317 may be found in Appendix K.

2/ Unidentified metabolites (8), none exceeding 0.5%. Percentage is total from organic fractions I, III, IV, and VII.

3/ Total of fractions I, III, IV, and VII.

Comments

Since no volatile traps were attached, evolving possible volatile degradation products could not be detected. Recovery rates were reported as ranges for each experiment and not for each sample analysis. Since % distribution of radioactivity was normalized from the total radioactivity recovered, actual % distribution is not known.

Data compiled and used in calculations/tabulations for the document, but not contained in this section need to be provided.

The reported estimated half-lives are different from those obtained by the reviewer.

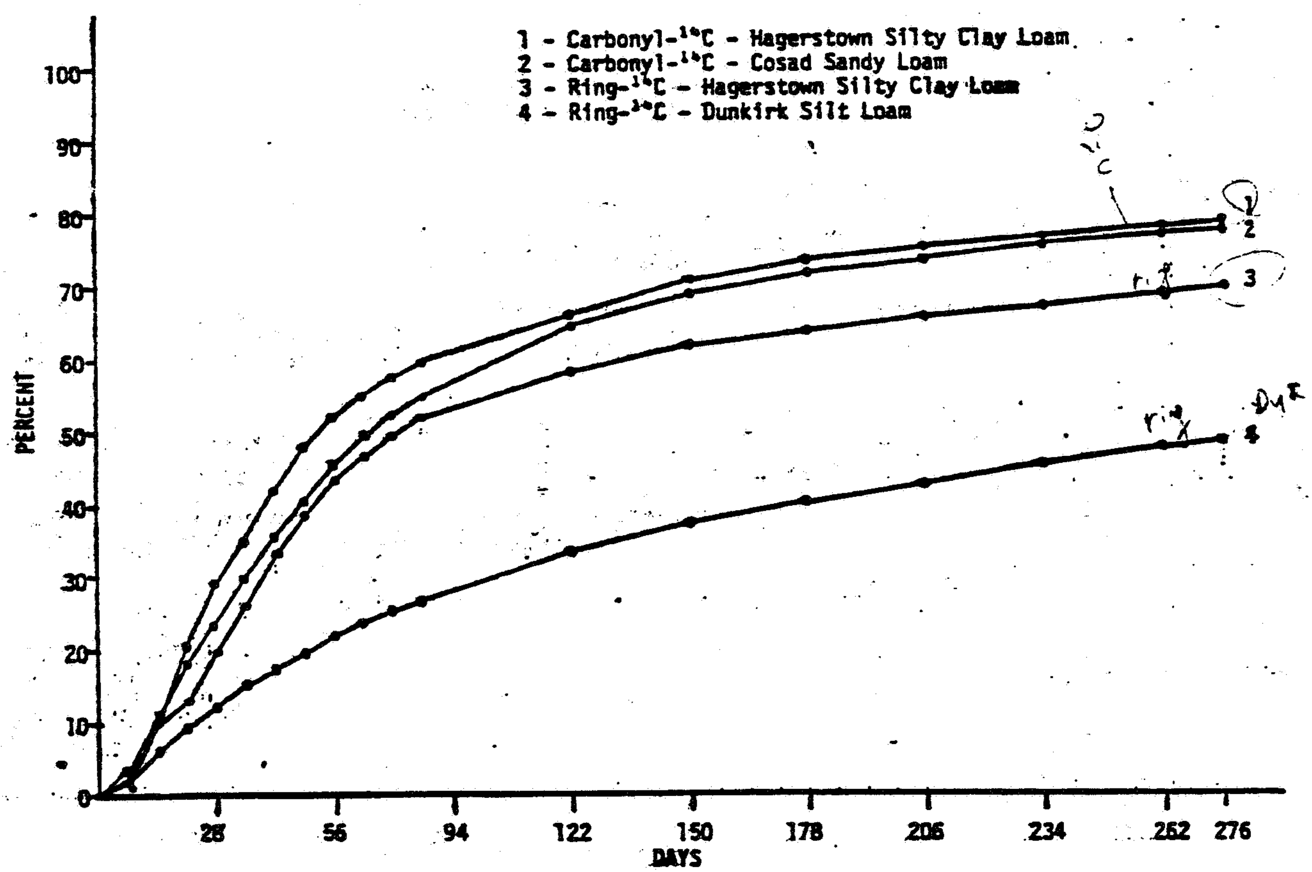
Conclusion

FMC 57020 degrades in soil under aerobic conditions to give CO_2 as a major product. The rate and degree of degradation vary with soil type with a half-life range of 56-173 days. Under anaerobic conditions, FMC 57020 degraded to FMC 65317.

Section 3.5

FIGURE 1

CUMULATIVE $^{14}CO_2$ EVOLUTION FROM SOILS



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3.6 Metabolism of Carbonyl-^{14}C FMC 57020 in a Sandy Loam Soil. T.A. Bixler, FMC Corp. P-0882 5/24/84, Rf. E3443, EPA Acc. No. 072819 (Rf. 7)

Experimental

This study was done with carbonyl-^{14}C FMC 57020 (14.58 mCi/mM, 98.2% pure) in Cosad sandy loam soil (properties of the soil are shown in section 3.5) for aerobic and anaerobic soil metabolism.

Soil samples were treated at 3.49 ppm (10.61 uCi) with carbonyl-^{14}C FMC 57020 in ethanol (200 ul) having a final specific activity of 135068 dpm/ug.

All the treatment conditions, extraction procedures and analyses were the same as described in Section 3.5.

Duplicate soil samples were taken at 0 time, 29, 60 and 90 days from the treatment. An anaerobic condition was established on day 30 of aerobic aging by flooding with water (degassed, distilled, pH 6.8). Dried alfalfa hay was mixed into each sample prior to flooding.

Results

The product distribution/material balance profile of carbonyl-^{14}C-FMC 57020 in Cosad sandy loam under aerobic conditions is summarized in table 1.

The recovery rate range of 92.0-96.7% was reported. No major product was found while several unindentified metabolites (8) were detected (none exceeding 1.2%). The half-life was calculated to be 28 days.

The analysis of Cosad sandy loam soil after 30 and 60 days under anaerobic conditions indicated that FMC 57020 was readily degraded to FMC 65317 (table 2) and no further mineralization was observed (CO_2 level remained the same as observed on day 29).

Recoveries based on 0-day (aerobic) analysis ranged from 88.6-90.9 %.

The percent distribution of several minor products as well as the major product, FMC 65317 and the parent compound is shown in table 3.

Comments

No traps for organovolatiles were used. However, the recovery (ranged 92.0-96.7% in the aerobic tests and 88.6-90.9 % in the anaerobic tests) was pretty good and indicates that little organovolatiles were evolved from the carbonyl-labeled compound.

TABLE 1
CARBONYL-^{14}C FMC 57020 - ANAEROBIC TEST
COSAD SANDY LOAM SOIL
MATERIAL BALANCE[1/]/PRODUCT DISTRIBUTION

	30 Day[2/]			60 Day[2/]		
	% Dist.	% 57020	% 65317	% Dist.	% 57020	% 65317
Water Layer						
$MeCl_2$ (VII)	20.8	0.6	17.8	21.5	0.1	19.7
Polar Aqueous (VIII)	10.2			11.4		
Soil Layer						
$MeCl_2$ (I)	17.0	1.9	13.0	15.2	0.6	13.4
MeOH (III)	2.7	0.8	0.8	3.1	0.8	0.8
EtOAc (IV)	3.8	1.2	0.7	3.8	0.8	0.8
Total FMC 57020		4.5			2.2	
Total FMC 65317			32.3			34.7
Other Products[3/]	7.5			6.7		
Total Organosolubles[4/]	44.3			43.6		
Polar Aqueous (VIII)	10.2			11.4		
Polar Aqueous (II,V)	6.5			6.6		
$^{14}CO_2$	27.6			26.5		
Bound Residues (VI)	11.4			11.9		
Total	100.0			100.0		

1/ Normalized percent distribution of total recovered ^{14}C. Recoveries based on 0 day aerobic test ranged from 88.6% - 90.9%. Residue levels (µg/g) of FMC 57020 and FMC 65317 may be found in Appendix I.

2/ Time following flooding of soil (60 and 90 days after treatment).

3/ Minor degradation products (12), none exceeding 0.7%. Percentage is total from organic fractions I, III, IV and VII (see Section III.C)

4/ Total of fractions I, III, IV and VII.

TABLE 2

PERCENT DISTRIBUTION OF PRODUCTS FROM 30 DAY[1/]

ANAEROBIC SOIL/WATER ORGANIC EXTRACTS

	$MeCl_2$[2/]	$MeCl_2$[3/]	MeOH[4/]	EtOAc[5/]
FMC 87015	0.1	0.2	-	0.1
FMC 83918	0.1	0.2	-	-
FMC 62632	0.1	0.1	-	-
FMC 65317	18.4	12.2	0.8	0.7
FMC 62667	0.5	0.4	-	-
FMC 60217	0.1	0.1	-	-
FMC 77039	0.1	0.1	-	-
FMC 55667	0.1	0.1	-	0.1
FMC 14788	-	<0.1	-	0.1
FMC 57020	0.7	1.5	0.8	1.1
FMC 55626	-	0.1	-	-
FMC 57061	-	-	-	-
Sub-Total	20.1	15.0	1.6	2.0
Unidentified	2.5	2.6	0.9	1.7
Total	22.6	17.6	2.7	3.7

1/ Data represents one interval from one of the replicate samples.
2/ $MeCl_2$ extract from water layer-Fraction VII.
3/ $MeCl_2$ extract from MeOH/water blend-Fraction I.
4/ Fraction III
5/ Fraction IV

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TABLE 3
CARBONYL-^{14}C FMC 57020-AEROBIC TEST
COSAD SANDY LOAM SOIL
MATERIAL BALANCE[1/]/PRODUCT DISTRIBUTION

	0 Time		29 Day		60 Day		90 Day	
	% Dist.	% 57020	% Dist.	% 57020	% Dist.	% 57020	% Dist.	% 57020
$MeCl_2$ (I)	95.7	94.1	45.1	43.4	19.6	18.6	8.0	7.5
MeOH (III)			8.0	6.4	4.9	4.2	3.2	2.3
EtOAc (IV)			3.7	1.2	3.9	1.4	3.3	0.9
Total FMC 57020		94.1		51.1		24.2		10.7
Unidentified Products[2/]	1.6		5.7		4.2		3.8	
Total Organosolubles	95.7		56.8		28.4		14.5	
Polar Aqueous (II, V)	0.1		3.7		4.3		4.1	
$^{14}CO_2$			27.5		50.9		62.5	
Bound Residues (VI)	4.2		12.0		16.4		18.9	
Total	100.0		100.0		100.0		100.0	

1/ Normalized percent distribution of total recovered ^{14}C. Recoveries based on 0 day data ranged from 92.0 -96.7%. Residue levels (ug/g) of FMC 57020 may be found in Appendix I.

2/ Unidentified metabolites (8), none exceeding 1.2%. Percentage is total from organic fractions I, III, and IV.

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An estimated half-life of 28 days under aerobic conditions was reported, but no half-life estimation was done under anaerobic conditions.

Conclusion

FMC 57020 is mineralized (evolving CO_2) under aerobic conditions with an estimated half-life of 28 days in Cosad sandy loam soil.

Under anaerobic conditions, FMC 57020 readily degrades to give FMC 65317 as a major product with an estimated half-life of about 13 days (reviewer's estimation).

This study is accepted for the aerobic/anaerobic soil metabolism data requirement.

3.7 Soil Mobility of FMC 57020, L.P. Kimme, FMC Corp. M-4862, 6191 1982, Rf. E1530: 70-135. EPA Acc. No. 248476 (Rf 31).

This study and the study in section 3.8 were previously submitted in connection with a request for an EUP but were not thoroughly reviewed by EAB because leaching studies were not required for an EUP at that time. However, a brief review (Dec. 3, 1982) of the leaching and adsorption data indicated that FMC 57020 has a potential to leach in the environment.

Experimental

The relative movement of methylene ^{14}C FMC 57020 (26.8 mCi/mM, 99.4% pure), atrazine, paraquat and 2,4-D in four soil types was determined by soil TLC and soil column chromatography.

The properties of the soil are summarized in table 1.

Table 1

Soils	Texture %			Organic Matter %	CEC[a]	pH	Bulk Density[b]
	Sand	Silt	Clay				
Leon fine sand	91.6	4.8	3.6	1.3	3.5	6.2	2.0
Cosad sandy loam	56.4	32.8	10.8	3.2	17.1	6.8	1.2
Dunkirk silt loam	24.8	60.0	15.2	2.3	10.9	4.8	1.2
Hagerstown clay loam	24.0	41.0	35.0	2.5	7.7	6.9	1.1

a/ Cation exchange capacity expressed in meq/100 g

b/ Expressed as g/cm³

Soil TLC Method: Each soil sample was air dried, sieved (250 u or 500 u) and was mixed with distilled water until a soil slurry was established. After TLC plates were made, they were air-dried overnight prior to spotting. The plates were developed in distilled water and were subjected to autoradiography.

The amount of chemical standard applied to each soil plate and the solvent in which it was dissolved are summarized in table 2.

Table 2

Standard	Solvent	ug	ul	dpm
Methylene-^{14}C FMC 57020	CH_2Cl_2	1.14	20	285,200
UL Ring-^{14}C Atrazine	CH_2Cl_2	3.24	30	277,170
Methylene-^{14}C Paraquat	H_2O	5.45	10	372,550
Carbonyl-^{14}C 2,4-D	CH_2Cl_2	0.425	15	228,495

Column Chromatography: Soil column chromatography of the four compounds was done only in Leon fine sand soil. Four glass columns (500 x 25 mm) packed with the soil (up to 30 cm) were saturated with distilled water. Three columns were used for ^{14}C FMC 57020 and the fourth was used for ^{14}C-atrazine. On top of the soil column, a glass wool plug was placed and then about 6 g of ^{14}C-treated soil were added. The actual radioactivity added is shown in table 3.

Table 3

Column #	Treatment	Wt. of Soil Plug	Total dpm
1	Methylene-^{14}C FMC 57020	5.84 g	12,339,803
2	"	5.91	12,487,712
3	"	5.96	12,593,361
4	UL Ring-^{14}C Atrazine	5.96	13,264,579

The columns were eluted with 250 ml (20 inches) of distilled water (5 ml fractions were collected for column #1 and 4, bulk sample for column #2 and 3).

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After elution, soil cores were removed in 6 cm sections from each column. Each treat soil plug was removed separately. After air drying and radioassay, the soil core samples were extracted with MeOH/water. The extract was concentrated, passed through Sep-Pak® with CH_2Cl_2, and subjected to HPLC analysis. Radioactivity in elute was determined.

Results

The R_f values of FMC 57020 and standard chemicals are summarized in table 4.

Table 4

Frontal Rf Determinations of FMC 57020 and Standard Chemicals on Soil

Soil Type	Chemical	Replicate Number 1	2	3	4	Mean	Std Dev
Leon fine sand	Paraquat	0.10	0.63	0.06	0.06	0.21	0.24
	Atrazine	0.75	0.69	0.75	0.74	0.73	0.02
	2,4-D	1.00	1.00	1.00	1.00	1.00	—
	FMC 57020	0.62	0.61	0.57	0.66	0.62	0.03
Cosad sandy loam	Paraquat	0.06		0.08		0.07	0.01
	Atrazine	0.30		0.39		0.35	0,05
	2,4-D	0.59		0.70		0.65	0.06
	FMC 57020	0.28	0.27	0.32	0.32	0.30	0.02
Dunkirk silt loam	Paraquat	0.05		0.04		0.05	0.01
	Atrazine	0.47		0.46		0.47	0.01
	2,4-D	0.61		0.61		0.61	—
	FMC 57020	0.34	0.29	0.33	0.28	0.31	0.03
Hagerstown clay loam	Paraquat	0.04		0.05		0.05	0.01
	Atrazine	0.47		0.44		0.46	0.02
	2,4-D	0.59		0.58		0.59	0.01
	FMC 57020	0.34	0.32	0.28	0.36	0.33	0.03

The soil TLC results show that FMC 57020 is categorized as low to intermediate (class 2-3) in Cosad sandy loam, Dunkirk silt loam and Hagerstown clay loam but mobile (class 4) in Leon fine sand.

The results obtained from the column chromatography is shown in table 5.

Table 5

% Vertical Distribution in Column

	FMC 57020					
	Col #1	**Col #2**	**Col #3**	**Mean**	**Std Dev**	**Col #4 Atrazine**
Treated soil plug	5.6	4.9	5.9	5.5	0.51	6.9
0-6 cm	6.5	5.5	4.5	5.5	1.00	3.7
6-12 cm	8.2	6.3	6.8	7.1	1.00	4.0
12-18 cm	10.3	12.3	9.7	10.8	1.40	5.1
18-24 cm	15.1	15.2	14.2	14.8	0.60	6.8
24-30 cm	20.2	16.3	19.3	18.6	2.00	8.4
Eluate	34.1	39.5	39.6	37.7	3.10	65.1
Total:	100.0	100.0	100.0	100.0	100.0	100.0

About 40% of radioactivity was found in the eluate and more than 30% was found in the bottom two sections of the columns in the ^{14}C-FMC 57020 experiments.

The HPLC analysis of soil segments and elute from the FMC 57020 test yielded mostly parent compound with a very low level (0.5%) of other products (2-4) (see table 6).

Conclusion

FMC 57020 appears to have a low to intermediate mobility in Cosad sandy loam, Dunkirk silt loam and Hagerstown clay loam but a high mobility in Leon fine sand. FMC 57020 has a potential to leach into ground water.

Table 6

FMC 57020 (Methylene-^{14}C)

Leon Fine Sand

Material Balance[a/]

Product	Treated Soil Plug	0-6 cm	6-12 cm	12-18 cm	18-24 cm	24-36 cm	Eluate	Total
FMC 57020	—	—	—	9.1	12.8	15.6	32.7	
Others[b,c/]	—	—	—	0.2	0.0	0.0	0.3	
Total % Extractable				9.3	12.8	15.6	33.0	70.7
Aqueous				0.6	1.1	1.9	1.1	3.7
PES				0.4	2.2	2.7		5.3
Total %	5.6	6.5	8.2	10.3	15.1	20.2	34.1	100.0
[b/]Number of other products				2			4	
[c/]Maximum % of highest single product				0.1			0.1	

[a/]Values represent percent of radioactivity

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3.8 Soil Adsorption/Desorption Characteristics of FMC 57020. L.W. Froelich, FMC Corp. Rf E1522, E1522, E 1896, 6/7/82. EPA Acc. No. 248476 (Rf 32).

Experimental

Using three concentrations of methylene-^{14}C-FMC 57020 solution in 0.01 M $CaCl_2$ (8.365 ug/236300 dpm/ml, 0.847 µg/23922 dpm/ml and 0.080 µg/2257 dpm/ml), adsorption-desorption studies were done in four soil types (described in section 3.7).

Ten milliliters of a solution was added to 2.5 g (oven dry weight) of each soil type in a 30 ml centrifuge tube (pre-weighed) and was shaken for 48 hours at 22-23°C. After centrifugation, a 0.1-0.5 ml aliquot was removed at 24 and 48 hours for LSC.

After weighing, each tube containing the soil and residual pesticide solution from the adsorption experiment was diluted with 10 ml of $CaCl_2$ equilibrated and radioassayed. Fresh $CaCl_2$ solution was made every 24 hours.

Results

The material balance was good (105.7%). The adsorption/desorption results from FMC 57020 are shown in tables 1 and 2.

Table 1

FMC 57020 Soil Isotherms - Adsorption

Soil Type	Adsorption - 24 Hours				Adsorption - 48 Hours			
	K	1/n	Q	Koc	K	1/n	Q	Koc
Cosad sandy loam	2.82	0.88	88	152	2.58	0.93	81	139
Dunkirk silt loam	6.85	0.81	326	562	7.42	0.82	353	608
Hagerstown silty clay loam	2.57	0.87	103	177	2.84	0.89	114	196
Leon fine sand	1.54	0.96	118	203	1.54	1.00	118	203

Table 2

FMC 57020 Soil Isotherms - Desorption

Soil Type	Desorption - 24 Hours				Desorption - 48 Hours			
	K'	1/n'	Q'	Koc'	K'	1/n'	Q'	Koc'
Cosad sandy loam	3.24	0.97	101	174	4.52	1.08	141	243
Dunkirk silt loam	12.13	0.88	578	994	17.06	0.91	812	1398
Hagerstown silty clay loam	4.10	0.91	164	283	6.50	1.00	260	448
Leon fine sand	4.21	1.11	324	554	15.99	1.28	1230	2104

Forty-eight hour adsorption constants (K) ranged 2.6 in sandy loam to 7.4 in silt loam while desorption constant (K') varied from 4.2 in sandy loam to 17 in silt loam.

Conclusion

FMC 57020 has a low soil binding potential, consequently has a high leaching potential.

3.9 Soil Mobility of FMC 57020 Aged Residues, L.P. Kinne, FMC Corp. P-0891, Rf. E3399, E3573, 6/6/84, EPA Acc. No. 072819 (Rf 10).

Experimental

Carbonyl-^{14}C FMC 57020 was aerobically aged on Cosad sandy loam (see section 3.5) for 60 days at room temperature before subjected to column leaching study.

The soil extraction procedure and subsampling are shown in figure 1. Radioassay was done on solid and liquid samples. All organosoluble fractions were dried over anhydrous Na_2SO_4 for HPLC injection.

Glass columns (50 x 2.5 cm) were packed to a height of 30 cm with Cosad sandy loam soil after the tips were plugged with glass wool. Another glass wool plug was inserted on top of the soil and then the columns were saturated with water before aged residue treatments (ca. 10g) were added. For a 0 day control, the soil was treated with 5 ppm of carbonyl-^{14}C-FMC 57020.

Total radiocarbon applied to each column appears as following:

Treatment	dpm	Elution Time (Hrs) R_1	R_2
FMC 57020 positive control	12,956,950	125	115
Aged soil sample (A)	2,542,371	182.5	197.5
Post Methanol Blend (B)	935,722	157.5	167.5
Post Soxhlet (C)	770,213	210	215
Post Acid Hydrolysis (D)	435,105	112.5	112.5

Each column was eluted with 250 ml of distilled water for 100-200 hours. Fractions were collected at 100 minute intervals, and radioassayed. The soil columns were then dissembled and the soil was removed in 6 cm segments. Each treated soil plug was removed separately. After air-drying, radioactivity was determined by combustion analysis.

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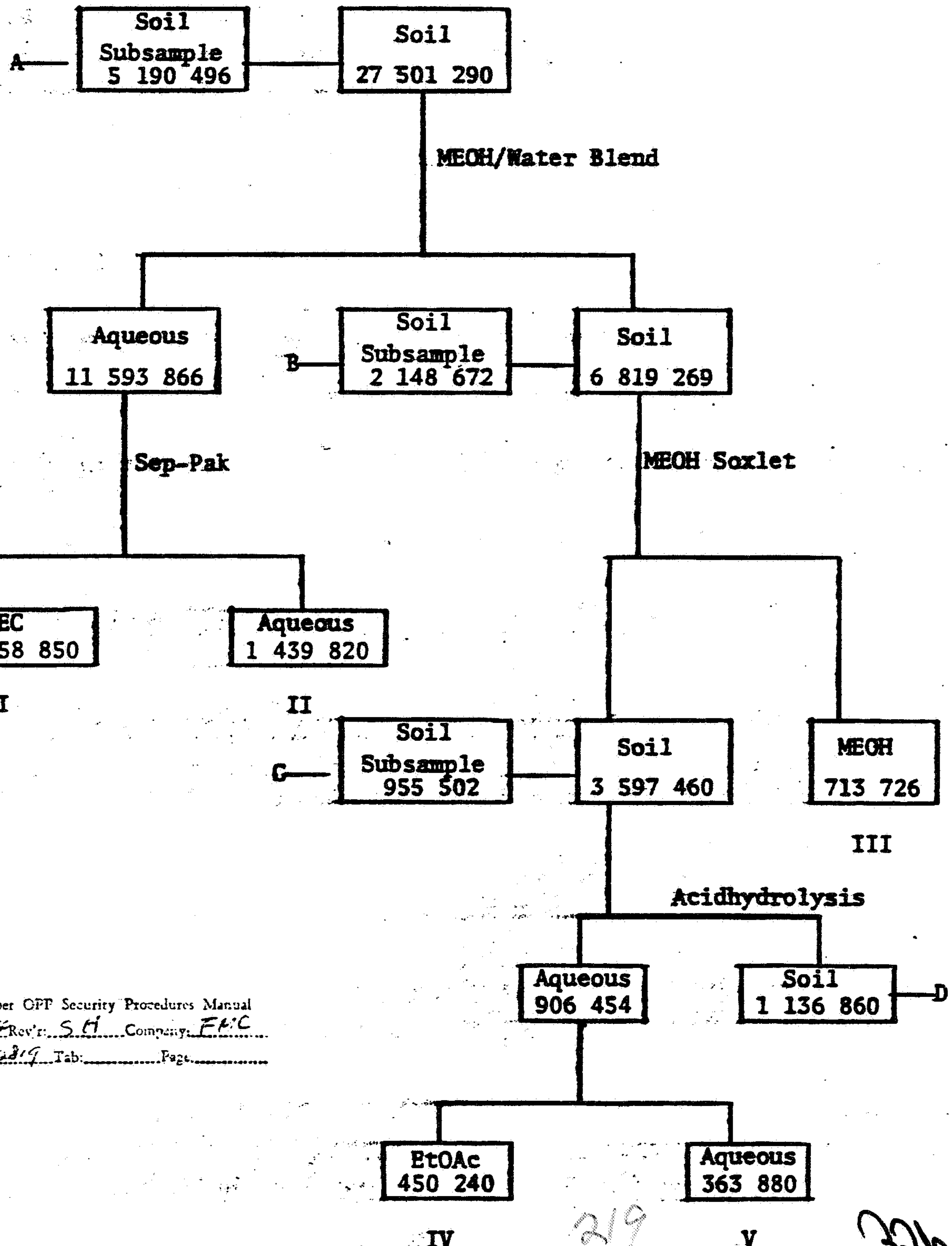
C. Soil Extraction and Subsampling

FIGURE 1
Soil Extraction Procedure



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Results

Recoveries were 69.3% for the 60 day aged soil and 87.2% for the 0 day control. The vertical distribution of all treatments are summarized in table 1.

Aged soil residues were more tightly bound to the soil than non-aged parent compound (ca. 30x). In the eluate, however, more residues were found for the aged soil than the 0-day control (about 3x). The rest of the radioactivity distribution among the columns was very similar to each other. The movement of soil bound residues (those remaining after extraction of FMC 57020) is expected to be negligible.

Comments

The radioresidue distribution after two months of aging in table 3 of Section 3.5 indicates that about 50% of radioactivity was mineralized. The rest of the radioactivity remaining on soil was distributed in FMC 57020 (ca. 35%), soil-bound residues (ca. 9%), unidentified organosolubles (ca. 3%) and polar compounds (ca. 3%).

Conclusion

The majority of the aged soil residues do not leach as much as parent FMC 57020. However, a small fraction of the aged residues leach more than the parent.

3.10 Soil Mobility of FMC 65317, A FMC 57020 Anaerobic Soil Degradate, L.P. Kimme, FMC Corp. P-0874, Rf. E3573, 4/25/84. EPA Acc. No. 072819 (Rf. 11).

Experimental

It has been shown that FMC 57020 is metabolized to FMC 65317 under anaerobic conditions (see sections 3.5 and 3.6). So the mobility of FMC 65317 on soil TLC plates was compared with that of parent compound and atrazine. Four soil types were used for the preparation of TLC plates as described in section 3.7.

The amount of chemical standard applied to each soil plate and the solvent in which it was dissolved are shown below.

Chemical	Solvent	ug	ul	Total dpm
Carbonyl-^{14}C FMC 57020	CH_3CN	0.93	15	240,182
UL-Ring-^{14}C Atrazine	CH_2Cl_2	3.31	10	282,879
Carbonyl-^{14}C FMC 65317	CH^2Cl_2	1.69	30	228,174

TABLE 1

FMC 57020 Aged Soil Leaching Study
^{14}C Vertical Distribution[1]

Description	FMC 57020 0 Day Control	A[2] 60 Day Aged Soil	B[2] 60 Day MEOH Blend	C[2] 60 Day Soxhlet	D[2] 60 Day Acid Digest
Extractable	-	-	51.9	55.2	59.2
Soil Plug[3]	1.2	33.0	34.3	36.0	36.6
0-6 cm	17.6	16.5	0.3	2.5	1.2
7-12 cm	48.3	34.6	4.1	1.3	1.4
13-18 cm	30.4	13.1	4.9	0.9	0.5
19-24 cm	1.5	0.5	0.8	0.4	-
25-30 cm	0.4	0.2	0.4	-	-
Eluate	0.7	2.1	3.3	3.7	1.1
TOTAL	100.1	100.0	100.0	100.0	100.0
Recovery[4]	87.0	69.3	106.2	96.5	102.6

[1] Normalized percent ^{14}C distribution.

[2] See extraction procedure in Figure 1.

[3] Soil containing residues that were applied to columns.

[4] Recovery of radiocarbon in soil and effluent based on dpm contained in soil fraction (Figure 1).

TLC procedures and autoradiography are the same as described in section 3.7. Four replicate analyses were conducted for FMC 65317 and two replicate analyses were done for FMC 57020 and atrazine.

Results

The Rf value determinations are summarized in the following table.

Soil Type	Chemical	Replicate 1	2	3	4	X̄	Std. Dev.
Cosad sandy loam	FMC 65317	0.50	0.62	0.54	0.55	0.55	0.05
	FMC 57020	0.20	0.21			0.21	<0.01
	Atrazine	0.31	0.27			0.29	0.03
Dunkirk silt loam	FMC 65317	0.69	0.69	0.65	0.68	0.68	0.02
	FMC 57020	0.22	0.19			0.21	0.02
	Atrazine	0.31	0.27			0.29	0.03
Hagerstown clay loam	FMC 65317	0.65	0.63	0.66	0.65	0.65	0.01
	FMC 57020	0.32	0.28			0.30	0.03
	Atrazine	0.45	0.41			0.43	0.03
Leon fine sand	FMC 65317	1.0	1.0	1.0	1.0	1.0	<0.01
	FMC 57020	0.75	0.73			0.74	0.01
	Atrazine	0.88	0.82			0.85	0.04

In all soil types, FMC 65317 showed higher mobility than FMC 57020.

Conclusion

FMC 65317, an anaerobic soil metabolite has a very high mobility in soil.

3.11 Mobility of FMC 57020 Residue in Soil. S. Witkonton, FMC Corp., P-0916, 7/31/84, Rf. E2P24:35-39, EPA Acc. No. 072819 (Rf. 12)

Experimental

A loamy sand plot (84% sand, 1.2% O.M. 120x150 ft) was treated with FMC 57020 4EC at 2.0 lb ai/a using a preplant incorporated application technique. The field received two major rainfall events plus one irrigation event and a total of 13.9 inches of water (rainfall plus irrigation) throughout the 61 day study period (table 1).

Soil samples at four depths (0-1, 1-2, 2-3 and 3-4 ft) were taken at 0, 3, 6, 11, 16, 21, 26, 31, 41, 51 and 61 days. A total of four cores per depth was composited to form the sample for each sampling day. The sampling scheme is outlined in figure 1. An untreated plot was sampled at 1 ft increments to 4 ft on days 0, 11, 21, 31 and 61.

The soil properties at each depth are summarized in table 2.

All soil samples were analyzed for residues of FMC 57020 and FMC 65317. Soil samples were extracted by hydrolyzing with 0.25N HCl followed by partitioning in hexane and washing with $NaHCO_3$. The hexane extract was quantitated for FMC 57020 with GC (figure 2). For the quantitation of FMC 65317, the acid hydrolysis solution was partitioned in ethyl acetate. The ethyl acetate solution was washed with $NaHCO_3$ and derivatized with pentafluoropropionic anhydride. The pentafluorophenyl FMC 65317 (PFA-FMC 65317) was quantitated by GC/MS at ion 352 (dechlorinated ion of PFPA-FMC 65317) (figure 3).

The method sensitivity for FMC 57020 and FMC 65317 in soil was validated to 0.10 ppm. Detection limit was 0.02 ppm for both compounds.

Untreated samples were fortified and average method recoveries were determined at 90 $\pm$ 13 and 87 $\pm$ 15% for FMC 57020 and FMC 65317, respectively. PFPA-FMC 65317 derivatization yield was 98%.

Results

All residues of FMC 57020 were found in the top 0-1 ft soil samples. No FMC 65317 were detected in any soil sample at any depth over the 61 day study period. Table 3 summarizes the average residues in soil.

TABLE 1

PRECIPITATION AND SOIL TEMPERATURE DATA

Days After Application	Calendar Time (Date)	Rainfall (Inches)	Irrigated Water (Inches)	Soil Temperature (°F)
	May 1984			
0	[illegible]	0	0	59
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	0.66	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	0.59	[illegible]	[illegible]
	June 1984			
[illegible]	[illegible]	0	[illegible]	[illegible]
40	[illegible]	0	0.50	[illegible]
[illegible]	[illegible]	0.44	[illegible]	[illegible]
44-47	16-19	1.14	[illegible]	[illegible]
51	23	0	[illegible]	[illegible]
52	24	0.18	[illegible]	[illegible]
53	25	0.29	[illegible]	[illegible]
56	28	0.16	[illegible]	[illegible]
58-59	6/30-7/1	0.38	[illegible]	[illegible]
	July 1984			
59	[illegible]	0	0	[illegible]
TOTAL WATER		11.18	3.50	

Figure 1
Sampling Plan

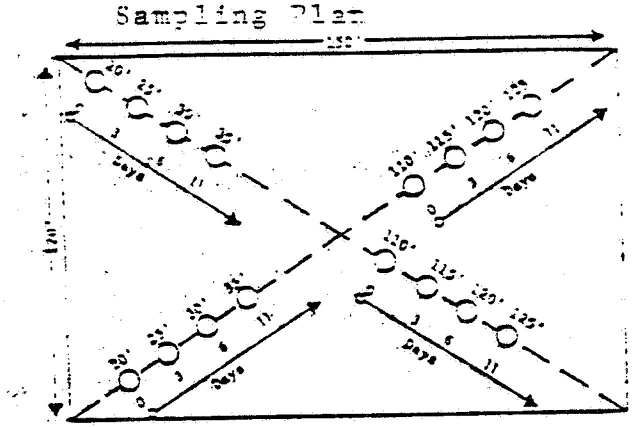

Table 2

SOIL CLASSIFICATION DATA
RIDER FARM, SHARPTOWN, MD

Soil Depth and (I.D.)	Soil pH	% Sand	% Silt	% Clay	% OM	Textural Class
0-1 Ft (A-1)	6.2	84.0	11.5	4.5	1.2	Loamy Sand
1-2 Ft (A-2)	5.5	85.0	9.0	6.0	0.1	Loamy Sand
2-3 Ft (A-3)	5.1	94.5	0.0	5.5	0.1	Sand
3-4 Ft (A-4)	4.9	97.0	0.0	3.0	0.0	Sand

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FIGURE 2

FMC 57020 SOIL METHOD FLOW CHART

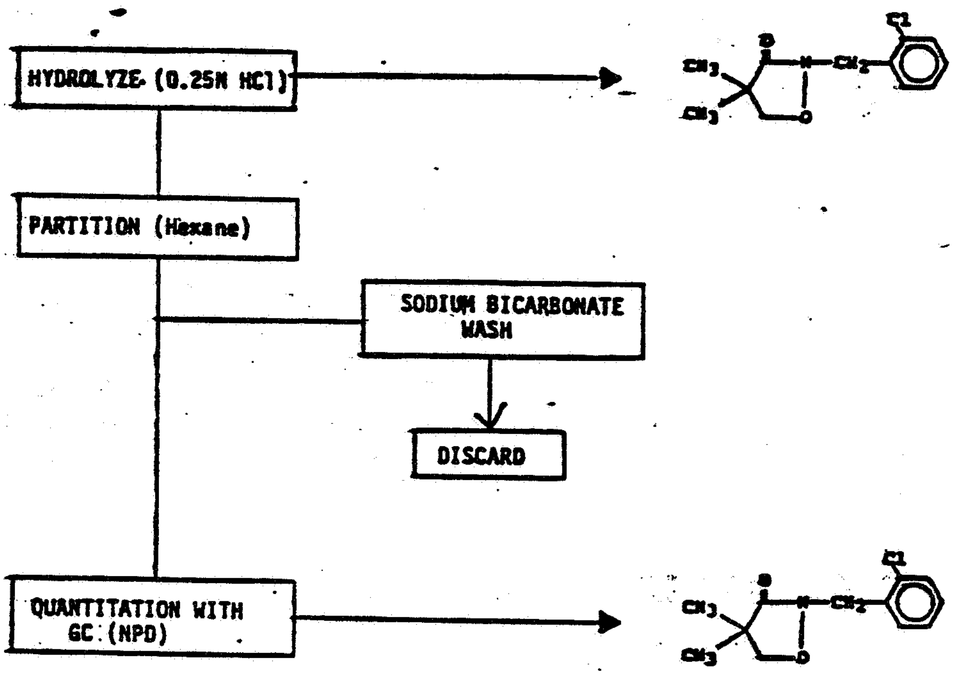

FIGURE 3

FMC 65317 SOIL METHOD FLOW CHART

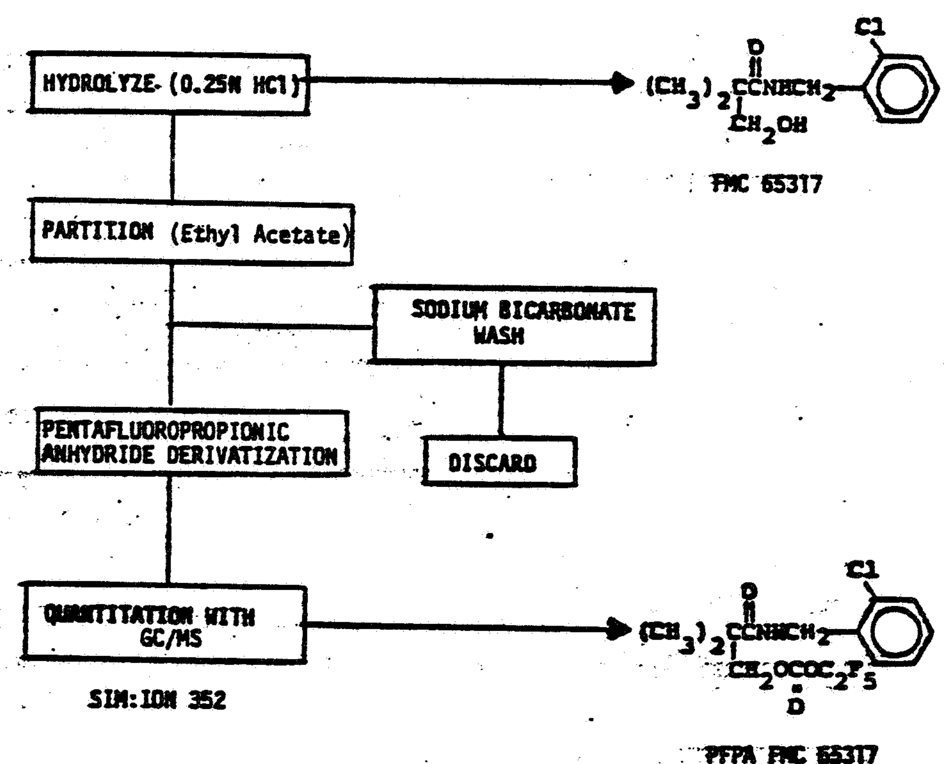

TABLE 3

SUMMARY OF AVERAGE RESIDUES[1/]

Days Lapsed	Sampling Depth (Ft)	Average Residue (ppm) FMC 57020	FMC 65317
0	0-1	0.80	ND
	1-2	ND	ND
	2-3	ND	ND
	3-4	ND	ND
3	0-1	0.38	ND
	1-2	ND	ND
	2-3	ND	ND
	3-4	ND	ND
6	0-1	0.22	ND
	1-2	ND	ND
	2-3	ND	ND
	3-4	ND	ND
11	0-1	0.12	ND
	1-2	ND	ND
	2-3	ND	ND
	3-4	ND	ND
16	0-1	0.25	ND
	1-2	ND	ND
	2-3	ND	ND
	3-4	ND	ND
21	0-1	0.10	ND
	1-2	ND	ND
	2-3	ND	ND
	3-4	ND	ND
26	0-1	0.13	ND
	1-2	ND	ND
	2-3	ND	ND
	3-4	ND	ND
31	0-1	0.16	ND
	1-2	ND	ND
	2-3	ND	ND
	3-4	ND	ND
41	0-1	0.23	ND
	1-2	ND	ND
	2-3	ND	ND
	3-4	ND	ND
51	0-1	0.20	ND
	1-2	ND	ND
	2-3	ND	ND
	3-4	ND	ND
61	0-1	0.14	ND
	1-2	ND	ND
	2-3	ND	ND
	3-4	ND	ND

1/ All average residue values were compiled from Table 5

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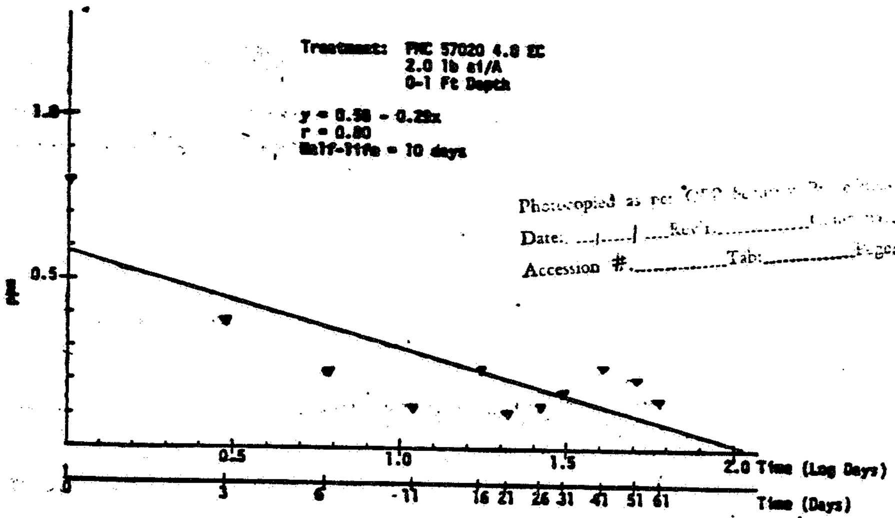
FMC 57020 residue in soil declined from 0.80 ppm at 0 time to 0.22 ppm at 6 day treatment time. Btween days 6 and 61, the residue level fluctuated between 0.10 and 0.25 ppm.

It was reported that a calculated half-life of 10 days was obtained for FMC 57020 (see figure 4).

Figure 4



Comments

The logarithmic scale plot of residue decline in figure 4 does not make sense. If the compound follows the first-order decay, the equation would be

$$C = C_o e^{-kt}$$

that is, $\ln C = -kt + \ln C_o$

So the plot would be made time vs log concentration. In figure 4, the plot was made with concentration vs. log time. Accordingly, the half-life of 10 days obtained is not valid.

The soil residue extraction procedure included a HCl reflux and an organic solvent partitioning (hexane for FMC 57020 and ethyl acetate for FMC 65317) and $NaHCO_3$ Wash. The following questions are raised:

1) Do FMC-57020 and FMC 65317 form respective salts with HCl?

2) If they do not form the salts, are they soluble enough to be extracted efficiently in water?

3) If they form salts, isn't it necessary to basify the acid extracts before partitioning in an organic solvent?

4) What was the $NaHCO_3$ wash for?

5) It was reported that the method sensitivity for FMC 57020 and FMC 65317 in soil was validated to 0.10 ppm and that the detection limit was 0.02 ppm for both compounds. However, in table 2 (table 4 in report) none of the residue levels were between 0.02 ppm and 0.1 ppm.

Conclusion

The leaching potential of FMC 57020 residues cannot be determined from this study until the registrant provides adequate explanations regarding the five questions above.

3.13 FMC 57020 Soil Mobility - PESTANS Modeling. F.D. Martin, FMC Corp. P-0904, 7/2/84, EPA. ACC. No. 072819 (Rf. 13).

This study was reviewed by Matthew Lorber, Agricultural Engineer, Environmental Processes and Guidelines Section/EAB.

In general, the FMC modeling study utilizing PESTANS was well done. The important first step of field validation was followed and this step is often overlooked in modeling studies. However, I would not consider the results conclusive and would recommend further modeling if FMC would like a modeling exercise to be part of their registration package. The reasons for recommending this are as follows:

- The version of PESTANS utilized by FMC is out dated and, in fact, incorrect. The updated version requires a further parameter, saturated hydraulic conductivity to describe the soil. As well, the degradation rate of the pesticide required as input to PESTANS has been described by Dr. Enfield as the "soil-based" decay rate, which differs from the "overall" decay rate which was input to the study by FMC. The decay rate input by FMC was 0.00446 hr^{-1} (according to my calculations, a half-life of 6 days translates to a decay rate of 0.0048 hr^{-1}). The soil based decay rate required by PESTANS to reflect a 6 day half-life should be 0.0090 hr^{-1}. Interestingly enough, a decay rate of 0.00446 hr^{-1} translates to a half-life of 11 days, so FMC modeled a slower decay rate than their field data indicated. The PESTANS run with

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the appropriate saturated hydraulic conductivity for a loamy sand (according to Dr. Enfield) and the appropriate decay rate showed results similar to FMC's results for the 30 day runs, although not for the right reasons. Attached are two PESTANS runs utilizing the parameters determined by FMC, including their decay rate of 0.00446 hr^{-1} and the proper decay rate of 0.0096 hr^{-1}. Specifically, both runs indicated that the pesticide would leach 18 cm at the end of a 30 day period, but not leach below 18 cm.

o For their long-term simulations, I do not agree with the parameters chosen for the sand soil. Although Dr. Enfield recommends parameters for a "sand" soil in the literature article describing PESTANS, and these were the input parameters used by FMC, these parameters also result in the prediction of a soil water content for sand of 24 % by volume. Sand soils used for agriculture can have water contents as low as 6 % and more typically have water contents in the range of 10-12 %. In discussions with Dr. Enfield, he informed me that these parameters were developed using measurements for several field soils which were described as "sand". He also indicated that a water content of 10 % can be generated in PESTANS by setting the characteristic curve coefficient to very low values (0.02) and also adjusting the porosity input. The water content significantly affects the leaching potential of a pesticide. With low water contents, incoming rainfall cannot be stored in the soil and will leach, resulting in more leaching of solute.

o Whereas PESTANS has its value in assessing the leaching potential of pesticides, it is rapidly being replaced by models which are more deterministic and realistic. These models typically operate on a daily time step and require actual rainfall and other weather information to determine more realistic time-varying recharge rates, rather than the hourly recharge rate used by PESTANS. For example, a spring applied pesticide can be subjected to intense spring weather. As much as 50 % of annually determined recharge can occur in the three months following application, before the time of significant chemical decay. This obviously can result in higher predictions of leaching than an assumption of steady recharge over the course of a year. However, this concern is minimal considering that FMC assumed much higher rainfall than can realistically be expected. I would recommmend that FMC contact Bob Carsel of the EPA Athens Research Laboratory and obtain a copy of Pesticide Root Zone Model - PRZM, for their further modeling studies.

Summary

- The modeling studies were well done considering that the PESTANS model was validated prior to long term simulations and that annual recharge for long term simulations were overestimated. Extrapolation to other soil types is a valid and useful approach.

- Unfortunately, the PESTANS model used by FMC was outdated and , in fact, incorrect. However, usage of the correct version would not lead to significantly different results.

- The sand soil charaterization in PESTANS is generous in favor of the registrant. I would not consider sand soil results reported valid, even if the correct version of PESTANS were used.

- The correct version of PESTANS should be obtained from Dr. Enfield. As well, PRZM shoud be used in place of PESTANS if possible.

3.14 Dissipation of FMC 57020 Residues in Soil. S. Witkonton and C. Long. FMC Corp. p-0896. Rf E2824:14-15, 6/13/84, EPA Acc. No. 072819 (Rf. 14).

Experimental

Residue trials in four sites (silt loam, IL and AR; sandy loam, NJ; sandy clay loam, NC) were conducted for soil dissipation studies with FMC 57020 4EC.

FMC 57020 4EC was applied to the soil as a pre-plant incorporated or pre-emergence treatment at 2.0 lb ai/a. Soil samples of 20 cores per plot at 0-6 and 6-12 inch depths were taken at about 0, 7, 14, 30, 60, 120, 150, 180, 360 and 500 days and analyzed for residues of FMC 57020. A detailed sample history is shown in table 1.

Rainfall records are presented in tables 2-9.

The soil samples were processed for analysis by air-drying to about 10 % moisture. The soil was then sifted, mixed and stored at 18°C until analysis.

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TABLE 1

SAMPLE HISTORY
FMC 57020 4.0 EC Application Rate: 2.0 lb ai/a

Location	Sample Identification	Type of Application	Day Interval
Raleigh, NC (Sandy Clay Loam)	MRY-444 MRY-445 MRY-446 MRY-447 MRY-518 MRY-684 PRZ-156 PRZ-157 PRA-25	PRE PPI	0, 7, 14, 30, 60, 152, 193, 323, 507
Penns Grove, NJ (Sandy Loam)	MRY-418 MRY-419 MRY-420 MRY-421 MRY-429 MRY-558 MRY-676 PRZ-75 PRA-42 MRY-677 PRZ-77	PRE PPI	0, 7, 14, 30, 60, 120, 180, 365, 514
Champaign, ILL (Silt Loam)	MRY-479 MRY-470 MRY-478 MRY-475 MRY-476 MRY-463 MRY-462 MRY-467 MRY-465 MRY-637 MRY-646 PRZ-16 PRZ-15 PRZ-58 PRZ-56 MRY-472 PRZ-262	PRE PPI	2, 9, 14, 30, 60, 120, 209, 366, 500
Marion, AR (Silt Loam)	MRY-493 MRY-494 MRY-499 MRY-669 MRY-663 MRY-497 MRY-661 PRZ-13 PRZ-105 PRZ-271	PRE PPI	0, 7, 15, 30, 58, 135, 166, 338, 498

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TABLE 2

PRECIPITATION DATA
PENNS GROVE, NJ

Month/Day/Year	Inches
May, 1982	
28	2.0
June, 1982	
1	0.05
4	0.08
5	0.01
6	0.08
7	0.09
13	2.00
16	0.01
22	0.02
29	0.03
30	0.06
Total	2.43
July, 1982	
3	0.09
23	0.03
27	2.90 1/
29	2.80 1/
30	0.01
Total	5.83
August, 1982	
5	0.03
8	0.07
10	0.03
17	0.06
23	0.08
25	0.03
Total	0.30
September, 1982	
3	0.04
20	0.07
23	0.08
27	1.00
Total	1.14
October, 1982	
19	0.02
25	1.80
Total	1.82
November, 1982	
1	1.05
13	1.02
15	0.01
24	0.03
28	1.04
30	0.05
Total	3.20
December, 1982	
3	0.01
6	0.07
12	0.05
16	0.07
19	0.01
25	0.01
30	0.05
Total	0.27

1/ Irrigated

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TABLE 3

PRECIPITATION DATA
PENNS GROVE, NJ

Month/Day/Year	Inches
January, 1983	
4	0.07
10	1.02
15	0.05
24	1.02
31	1.00
Total	3.16
February, 1983	
2	0.05
11	15.0 (snow)
17	0.01
23	0.03
Total	15.09
March, 1983	
1	0.08
7	0.03
9	0.07
10	0.03
12	0.01
18	1.02
21	2.03
27	1.02
Total	4.29
April, 1983	
2	0.07
7	0.02
8	0.02
10	1.08
15	2.50
19	0.01
24	1.04
Total	4.74
May, 1983	
4	0.04
15	0.03
16	1.03
20	0.01
21	1.00
22	0.09
24	0.01
26	1.02
27	0.02
30	0.06
Total	3.31
June, 1983	
2	0.02
4	0.01
19	0.03
21	1.09
28	1.04
Total	2.19
July, 1983	
17	1.02
19	0.02
Total	1.04
August, 1983	
5	0.03
11	1.03
17	0.01
22	0.02
29	0.06
Total	1.15
September, 1983	
12	0.09
13	0.01
15	1.00
21	2.50
23	0.01
Total	3.61
October, 1983	
12	0.08
19	0.04
23	1.50
Total	1.62

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TABLE 4

PRECIPITATION DATA
MARION, AR

Month/Day/Year	Inches
June, 1982	
3	0.19
4	0.35
10	0.52
13	0.22
16	1.68
23	0.22
26	0.80
28	0.12
29	0.28
Total	4.38
July, 1982	
1	0.15
2	0.47
11	0.05
20	0.20
23	1.76
26	0.46
27	0.02
31	0.37
Total	3.48
August, 1982	
1	0.11
15	2.31
16	1.05
25	0.02
30	0.35
Total	3.84
September, 1982	
13	1.32
16	0.04
18	0.31
Total	1.67
October, 1982	
7	0.72
8	0.04
9	0.25
10	0.02
12	0.15
13	0.05
20	0.15
30	0.05
Total	1.43
November, 1982	
2	0.20
3	0.08
12	0.24
17	0.12
18	0.05
19	0.10
20	1.54
21	1.00
22	0.01
23	0.07
24	0.04
28	1.70
Total	5.78
December, 1982	
3	0.68
4	3.48
5	0.37
11	0.71
15	2.13
22	0.03
23	0.12
25	3.40
26	1.52
27	2.16
28	0.93
31	15.53
Total	31.06

TABLE 5

PRECIPITATION DATA
MARION, AR

Month/Day/Year	Inches	Month/Day/Year	Inches
January, 1983		March, 1983	
3	0.28	5	1.44
10	0.06	6	0.08
21	0.60	17	0.24
22	0.29	18	0.01
23	0.11	20	0.12
24	0.20	27	0.33
29	0.46	30	0.15
30	0.02	Total	2.37
Total	2.02	April, 1983	
February, 1983		2	0.84
1	0.61	3	0.09
2	0.25	5	1.22
6	0.59	6	0.09
9	0.30	7	0.72
22	0.12	8	0.34
23	0.30	9	0.06
28	0.06	13	0.09
Total	2.23	14	1.30
		18	0.50
		22	0.25
		24	1.98
		30	0.24
		Total	7.72

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TABLE 6

PRECIPITATION DATA
CHAMPAIGN, IL

Month/Day/Year	Inches
June, 1982	
14	1.02
15	0.22
18	1.11
19	0.14
22	0.04
28	0.07
29	0.10
Total	2.70
July, 1982	
3	3.82
10	0.37
18	0.02
19	0.02
21	1.02
22	0.01
28	0.25
Total	5.51
August, 1982	
5	1.09
7	0.01
8	0.21
10	0.11
20	0.22
23	0.01
24	0.71
26	0.07
30	0.29
31	0.05
Total	2.77
September, 1982	
1	0.77
2	0.03
6	0.01
13	0.22
14	0.04
17	0.37
23	0.01
25	0.02
Total	1.47

Month/Day/Year	Inches	
October, 1982		
3	0.02	
6	0.96	
7	0.03	
8	0.10	
9	0.07	
19	1.03	
20	0.14	
28	0.03	
29	0.07	
31	0.56	
Total	3.01	
November, 1982	Rain	Snow
1	0.63	0
2	0.11	0
4	0.01	0.1
11	0.23	0
12	0.43	0
19	0.54	0
20	0.58	0
21	0.15	0
22	0.02	0
23	0.37	0.2
25	0.02	0
26	0.29	0
27	0.08	0
28	0.87	0
Total	4.33	0.3
December, 1982		
1	0.02	0
2	0.37	0
3	0.90	0
4	0.40	0
5	0.18	0
8	0.01	0
10	0.37	1.6
14	0.02	0
24	1.29	0
25	0.30	0
27	0.52	0
Total	4.38	1.6

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TABLE 7

PRECIPITATION DATA
CHAMPAIGN, IL

Month/Day/Year	Inches	Snow
January, 1983		
9	0.02	0
10	0.02	0
11	0.04	0.4
21	0.11	0.3
22	0.34	1.1
23	0.11	1.0
26	0.02	0.2
29	0.08	0
Total	1.46	
February, 1983		
1	0.31	0
2	0.64	0.4
3	0.07	0.6
5	0.01	0.1
6	0.10	1.1
24	0.02	0.1
Total	1.15	
March, 1983		
5	0.20	0
6	0.31	0
7	0.42	0
9	0.05	0.5
10	0.07	0.8
20	0.88	7.6
26	0.13	0
27	0.26	0.2
28	0.03	0
31	0.01	0
Total	2.36	
April, 1983		
1	0.73	
2	0.29	
3	0.07	
4	0.02	
5	0.20	
6	0.17	
7	0.05	
8	0.02	
9	0.59	
10	0.10	
12	0.11	
13	1.34	
14	0.19	
16	0.03	
27	1.14	
28	0.46	
29	0.06	
30	0.84	
Total	6.41	

Month/Day/Year	Inches
May, 1983	
1	2.4
3	0.16
7	0.01
12	0.02
13	1.60
14	0.15
19	0.80
23	0.38
25	0.02
28	0.77
30	0.02
Total	6.33
June, 1983	
3	0.70
4	0.10
6	0.14
14	0.77
19	0.88
27	0.20
28	0.10
30	0.87
Total	3.76
July, 1983	
3	0.44
29	0.48
30	1.05
Total	1.97
August, 1983	
3	0.34
9	0.26
17	0.65
22	0.55
25	0.55
26	0.95
Total	3.30
September, 1983	
6	0.30
21	0.42
Total	0.72
October, 1983	
12	1.07
14	0.20
20	1.35
21	1.70
22	1.86
Total	6.18

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TABLE 8

PRECIPITATION DATA
RALEIGH, NC

Month/Day/Year	Inches
June, 1982	
26	1.36
27	0.30
Total	1.66
July, 1982	
4	2.50
5	0.33
12	0.67
23	0.95
28	0.20
29	0.16
31	0.23
Total	5.04
August, 1982	
1	0.96
8	0.18
9	1.08
11	0.27
12	0.05
Total	2.54
September, 1982	
18	0.05
19	0.20
21	0.47
22	0.01
26	0.77
Total	1.50
October, 1982	
9	0.03
13	1.25
14	0.20
23	1.75
24	0.37
Total	3.60
November, 1982	
4	0.87
12	0.13
13	0.48
14	0.05
15	0.32
27	0.03
28	0.34
29	0.11
30	0.01
Total	2.34
December, 1982	
1	0.50
5	0.02
6	0.03
11	0.84
12	0.90
16	0.84
19	0.12
28	0.01
29	0.25
30	0.33
31	0.18
Total	4.02

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TABLE 9

PRECIPITATION DATA
RALEIGH, NC

Month/Day/Year	Inches
January, 1983	
2	0.20
3	0.23
4	0.01
5	0.37
9	0.01
10	0.02
12	0.02
21	0.16
22	0.67
27	0.09
28	0.01
Total	1.79
February, 1983	
2	1.44
6	0.94
10	0.76
11	0.60
14	1.04
22	0.05
23	0.55
24	0.28
25	0.12
26	0.01
28	0.21
Total	6.00
March, 1983	
1	0.65
6	1.26
7	0.23
8	0.03
9	0.01
10	0.01
11	0.07
17	0.69
18	3.17
21	0.27
24	0.73
27	0.27
30	0.10
31	0.29
Total	7.78
April, 1983	
2	0.18
5	0.02
6	0.02
7	0.04
8	0.20
9	0.11
10	0.04
15	2.22
18	0.23
23	0.28
24	0.20
	3.54

Month/Day/Year	Inches
May, 1983	
3	0.39
4	0.06
8	0.01
13	0.02
14	0.79
16	0.48
20	1.16
21	0.73
22	0.59
23	0.74
26	0.38
27	0.52
29	0.01
30	0.01
Total	5.89
June, 1983	
1	0.20
4	0.65
7	1.30
21	0.20
29	0.40
30	0.01
Total	2.76
July, 1983	
5	0.30
22	0.60
23	0.15
25	0.30
Total	1.35
August, 1983	
3	0.30
10	0.40
Total	0.70
September, 1983	
14	0.95
23	0.10
Total	1.05
October, 1983	
6	0.15
13	0.67
22	0.15
23	0.95
Total	1.92

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The 0-6 inch depth soil classification data are shown in table 2.

Table 10

SOIL CLASSIFICATION DATA
0-6 INCH DEPTH

Location	Soil pH	% Sand	% Silt	% Clay	% OM	CEC meg /100 g	Textural Class
Champaign, IL	5.6	26.4	59.6	16.0	2.5	18.7	Silt loam
Marion, AR	6.4	32.8	44.8	22.4	0.6	8.7	Silt loam
Raleigh, NC	5.9	52.4	14.4	33.2	3.2	3.1	Sandy clay loam
Penns Grove, NJ	6.0	71.6	18.8	9.6	1.5	4.5	Sandy loam

The soil samples were extracted as described in section 3.11 by hydrolyzing with HCl, partitioning in hexane and washing with $NaHCO_3$. The hexane extract was quantified for FMC 57020 with GC.

Method Sensitivity and detection limit were the same as in section 3.11.

Untreated sample was fortified with FMC 57020 solution (0.01 or 0.25 ug/ul) prior to any analytical manipulation and the recovery averaged 83 $\pm$ 14 % for all the samples except those collected on days 7 and 500. Average recovery for those samples was 82 $\pm$ 7 %.

Results

Actual residue levels of FMC 57020 found in the top 6 inch and 6-12" level are presented in tables 5-8.

Comments

The report says that "due to the rapid exponential decline of FMC 57020 residues linear regression equation yields a best fit line when ppm values are plotted against days expressed as a logarithmic scale (figures 2-5)". All of half-life estimations were done according to the plots. Please explain the mathematical equations in terms of log time and concentration. Also, see the comments in section 3.11.

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TABLE 5

SUMMARY OF AVERAGE FMC 57020 RESIDUES
CHAMPAIGN, IL
(Silt Loam)

Days Lapsed	Average Soil Residues, ppm[1/] FMC 57020			
	0-6 Inches		6-12 Inches	
	PRE	PPI	PRE	PPI
2	1.12	0.77	0.10	(0.06)[2/]
9	0.78	1.01	(0.05)	(0.03)
14	0.56	0.72	(0.05)	(0.04)
30	0.40	0.58	(0.02)	(0.05)
60	0.26	0.35	ND	(0.02)
120	0.24	0.36	ND	ND
209	0.10	0.26	ND	ND
366	(0.06)	0.16	ND	ND
500	(0.09)	0.10	ND	ND

TABLE 6

SUMMARY OF AVERAGE FMC 57020 RESIDUES
PENNS GROVE, NJ
(Sandy Loam)

Days Lapsed	Average Soil Residues, ppm[1/] FMC 57020			
	0-6 Inches		6-12 Inches	
	PRE	PPI	PRE	PPI
0	1.72	1.42	0.52	0.24
7	0.68	1.11	(0.04)[2/]	0.13
14	0.51	0.59	(0.02)	(0.04)
30	0.51	0.57	(0.04)	(0.08)
60	0.33	0.38	ND	0.14
120	0.16	0.16	ND	(0.04)
180	0.13	0.14	(0.04)	(0.06)
365	(0.02)	(0.04)	(0.02)	(0.02)
514	ND	(0.03)	ND	ND

58.7 56.2

ND = None Detected

1/ Corrected for average method recovery

2/ Numbers enclosed in parentheses are estimated levels above method detectability (0.02 ppm) and less than method sensitivity (0.10 ppm)

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TABLE 7

SUMMARY OF AVERAGE FMC 57020 RESIDUES - RALEIGH, NC (Sandy Clay Loam)

Days Lapsed	Average Soil Residues, ppm[1/] FMC 57020			
	0-6 Inches		6-12 Inches	
	PRE	PPI	PRE	PPI
0	0.54	0.72	0.22	0.30
7	0.68	0.41	(0.06)[2/]	(0.07)
14	0.32	0.26	(0.03)	(0.02)
30	0.36	0.30	(0.05)	(0.08)
60	0.22	0.32	0.16	ND
152	(0.08)	(0.09)	ND	ND
193	(0.06)	0.11	ND	ND
323	(0.08)	(0.06)	ND	ND
507	(0.04)	(0.04)	ND	ND

TABLE 8

SUMMARY OF AVERAGE FMC 57020 RESIDUES MARION, AR (Silt Loam)

Days Lapsed	Average Soil Residues, ppm[1/] FMC 57020			
	0-6 Inches		6-12 Inches	
	PRE	PPI	PRE	PPI
0	0.80	0.64	0.12	(0.03)[2/]
7	0.57	0.54	ND	(0.05)
15	0.44	1.04	ND	(0.08)
30	0.44	1.13	(0.03)	(0.08)
58	0.34	0.38	(0.08)	(0.08)
135	0.10	0.12	(0.02)	(0.03)
166	(0.07)	(0.09)	ND	(0.04)
338	(0.04)	(0.08)	ND	ND
498	(0.03)	(0.06)	ND	ND

ND = None Detected

1/ Corrected for average method recovery

2/ Numbers enclosed in parentheses are estimated levels above method detectability (0.02 ppm) and less than method sensitivity (0.10 ppm)

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FIGURE 2

CHAMPAIGN, IL
Silt Loam Soil

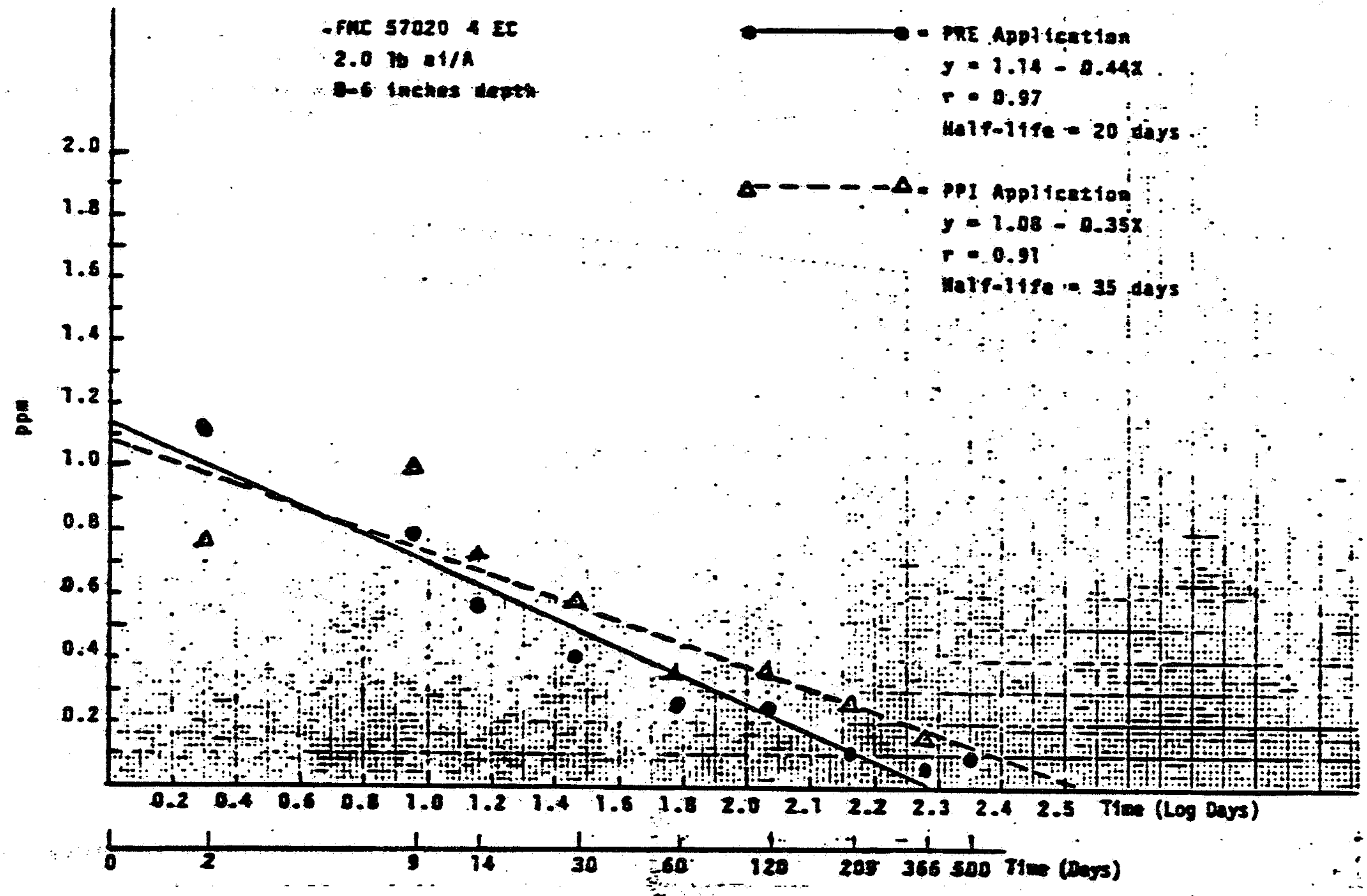

FIGURE 3

PENNS GROVE, NJ
Sandy Loam Soil

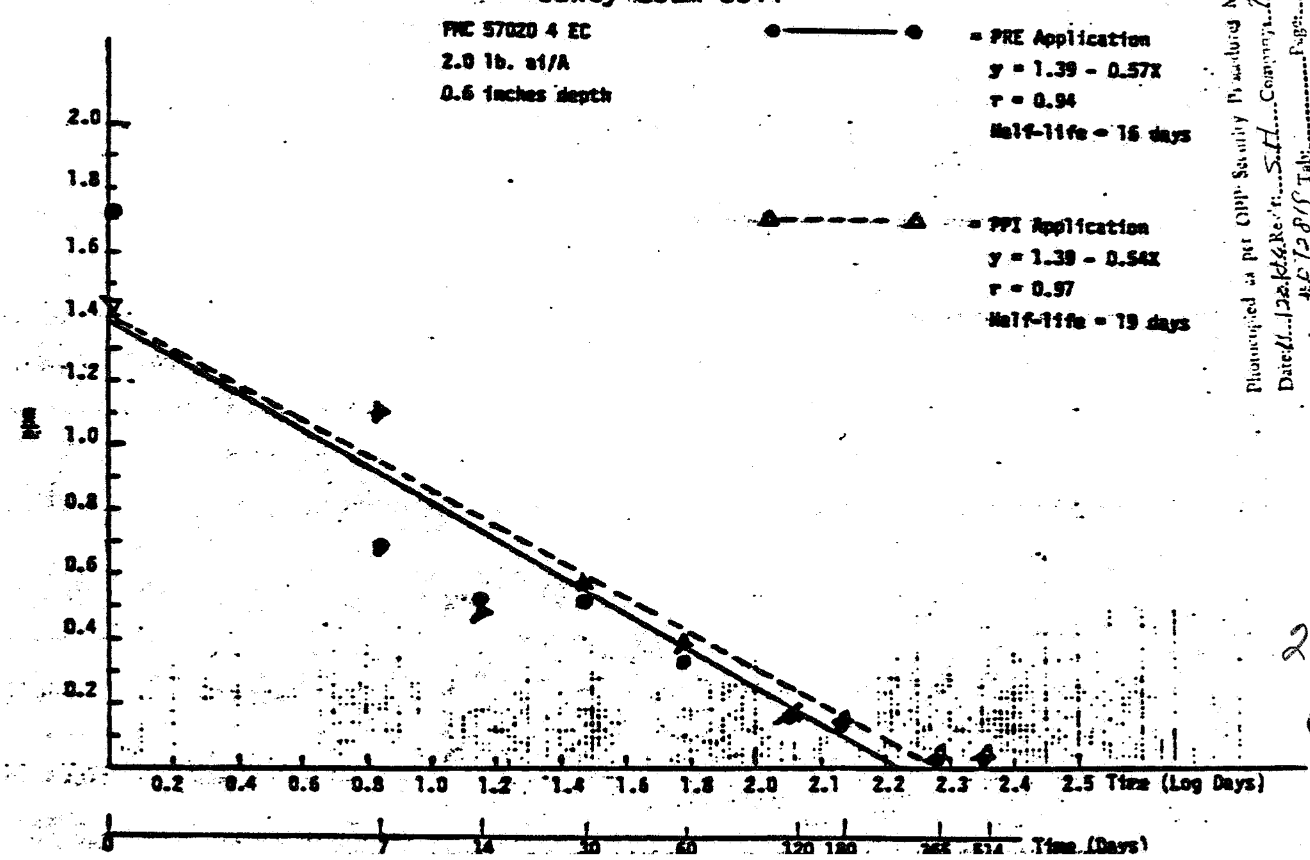

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FIGURE 4

RALEIGH, NC
Sandy Clay Loam Soil

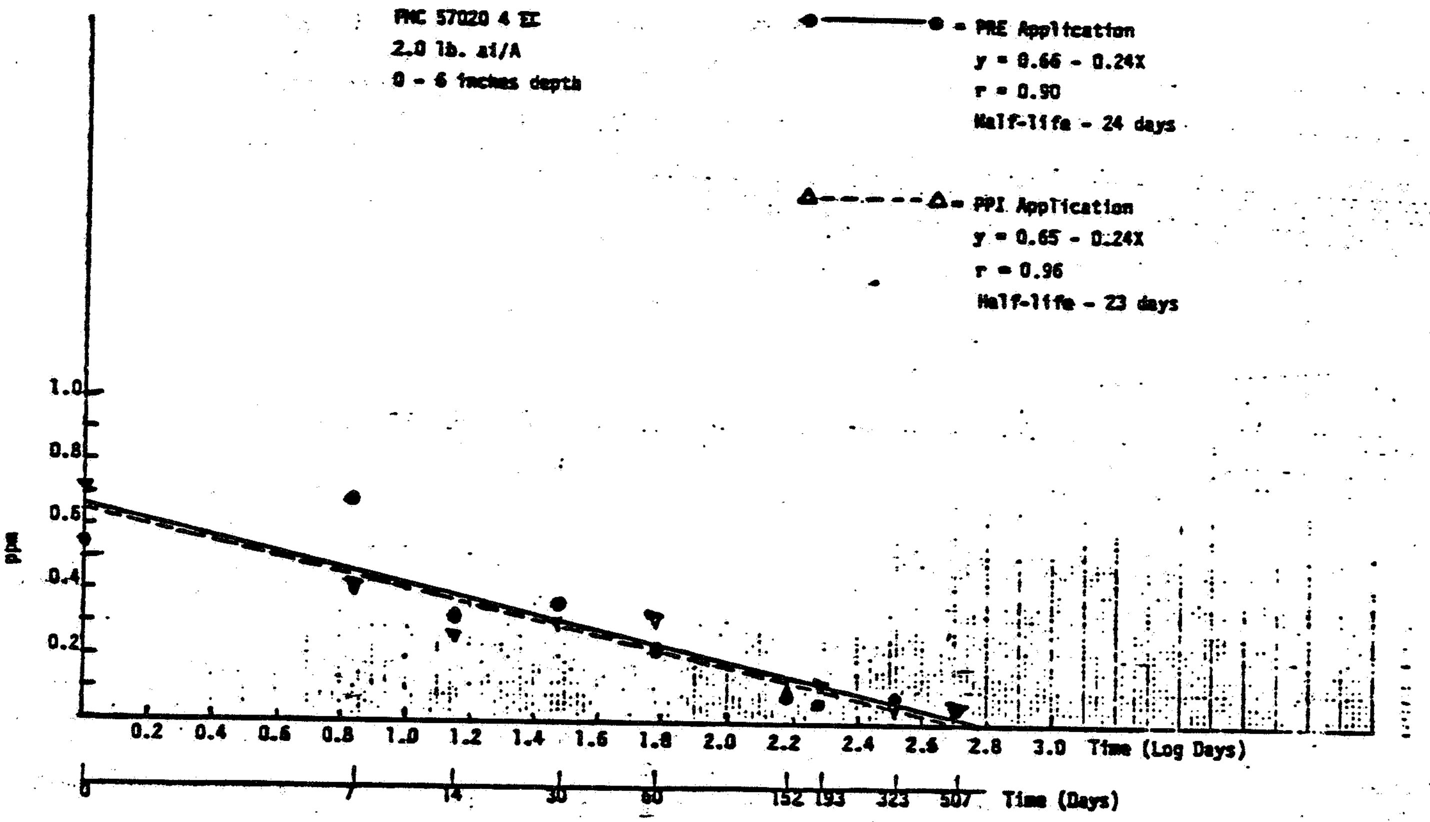
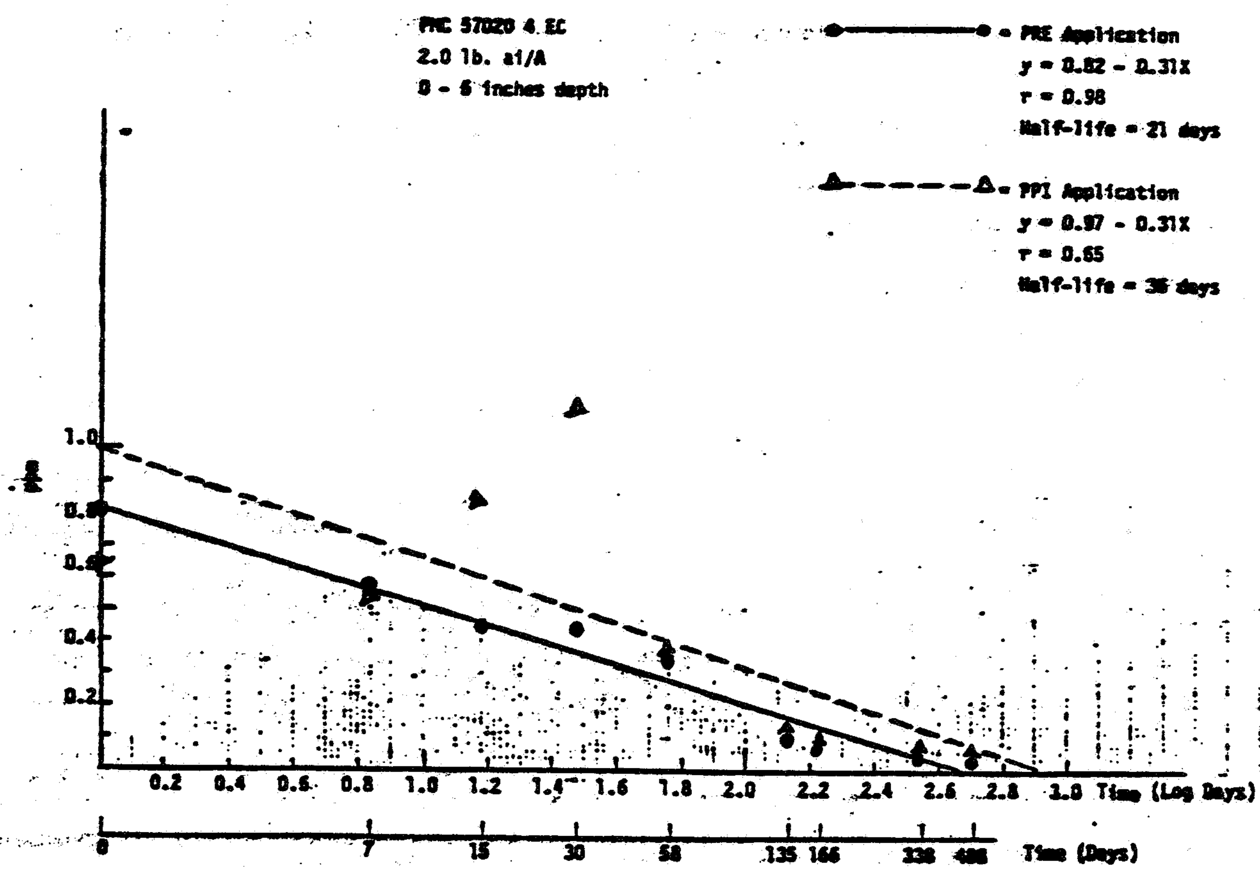


FIGURE 5

MARION, AR
Silt Loam Soil



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Conclusion

This study cannot be accepted for the following reasons:

- The registrant should re-plot/re-calculate the half-lives.

- For the half-life calculations, FMC 57020 levels in soils deeper than 6 inches should also be considered.

- Since there were indications that FMC 57020 is leaching, sampling should have been done at depths deeper than 12 inches.

3.15 Uptake of Soil-Aged ^{14}C Labeled FMC 57020 Residues into Outdoor Rotational Crops - 10 Month Interval. S.F. El-Nagger, J.L. Reynolds, FMC Corp. P-0871, 5/11/84, Rf E2238:1-115, E3366:27-40, EPA Acc. No. 072819 (Rf. 15).

Experimental

After ^{14}C FMC 57020 (ring labeled, 1.97 mCi/mM, 98.6%; carbonyl labeled, 2.09 mCi/mM, 97.1% pure) was sprayed at 19.7-21.4 mg ai/sq ft using an Anaspra Aerosol sprayer, the soil in each test plot (1 x 10 ft, sand, 25.2%; silt, 56.8 %; clay, 18.0 %, 3.3 % O.M.) was hand tilled to a depth of 4" and soybeans were planted (6/16/82) in rows about 2" deep. Soybeans were harvested after 118 days.

Ten months (310 days) after chemical application, the plots were hand tilled to a depth of 4". Rotational crops consisting of corn, oats, cabbage and sugar beets were planted (4/26/83). Corn, oats, and sugar beets were direct seeded while 3-week old cabbage plants were transplanted. Additional crops were planted outside the treated area for control samples.

Triplicate soil samples (0-6" and 6-12") were randomly collected from each plot prior to planting (10 months) and harvesting (16 months) the last rotational crop.

Rotational crop sampling was done at 45 days (oats, cabbage and corn) and at 85 days (sugar beets) for immature plants and at 97 days (oats and cabbage), 113 days (corn silage) and 167 days (corn and sugar beet crops) for mature plants. Plants were combined according to type and ^{14}C label.

All plant samples (except mature oats and corn) were frozen in liquid nitrogen, chopped and ground. Mature oats were separated into grain and straw while corn was separated into grain and stover. The two grain samples were just ground. Subsamples were taken in triplicate and radioassayed by combustion analysis.

Radioresidue in soil samples was determined by radioactivity in post extraction solids and radioactivity in MeOH/water extracts. All radioassay was done in triplicate.

The extraction and purification schemes for soils and crops are shown in figures 1 and 2.

The acetonitrile fraction (xx) (fig. 1) from the rotational crop was analyzed by HPLC along with known analytical standards. Concentrated CH_2Cl_2 (VIII) from the soil extraction procedure (fig. 2) was isotopically diluted with unlabeled FMC 57020 and analyzed by HPLC.

Concentrated organosoluble extracts (VIII, X, XII) (fig. 2) from the soil extraction were subjected to TLC (Analtech silica-gel GC, 250u, $CHCl_3$: MeOH = 98 : 2) and autoradiography. The purified organosoluble extracts (XX) (fig. 1) from the sugar beet tops and oat straw were spotted on either Analtech silica-gel CF, 250u or Quanta/Gram silica gel GF, 250u.

Results

Radioactivity levels in the immature rotational crops ranged 0.05-0.1 ppm for both labels (table 1).

Table 1

TOTAL ^{14}C RESIDUE (PPM[1/]) CONTENT IN IMMATURE ROTATIONAL CROPS

Rotational Crop	FMC 57020	
	Carbonyl-^{14}C	Ring-^{14}C
Corn	0.094	0.077
Oats	0.092	0.098
Cabbage	0.090	0.073
Sugar Beet Top	0.047	0.061
" " Beet	0.046	0.064

1/ ppm (µg/g) equivalent to FMC 57020

In the mature rotational crops, oat straw and grain showed the highest ^{14}C residues (0.07 0.12 ppm). The total ^{14}C residue levels in rotational crops are shown in table 2 and ^{14}C residue distribution is shown in tables 3 and 4.

TABLE 2

TOTAL ^{14}C RESIDUE (PPM[1/]) CONTENT IN MATURE ROTATIONAL CROPS

Crop	FMC 57020 Carbonyl-^{14}C	FMC 57020 Ring-^{14}C
Corn		
Silage	0.013	0.016
Stover	0.028	0.045
Grain	0.016	0.019
Oats		
Straw	0.071	0.118
Grain	0.070	0.085
Cabbage	0.032	0.022
Sugar Beet		
Top	0.042	0.063
Beet	0.021	0.032

[1/] ppm (µg/g) equivalent to FMC 57020

TABLE 3

^{14}C RESIDUE DISTRIBUTION IN DIFFERENT FRACTIONS FROM CARBONYL-^{14}C FMC 57020 APPLICATION (2 lb/a)

	Corn						Oats				Sugar Beets				Cabbage	
	Silage		Stover		Grain		Straw		Grain		Tops		Beets			
Fraction	%	(ppm)	%	(ppm)	%	(ppm)	%	(ppm)	%	(ppm)	%	(ppm)	%	(ppm)	%	(ppm)
Hexane (IV)	--	--	1.5	(0.001)	4.7	(0.001)	0.9	(0.001)	2.2	(0.002)	0.6	(0.000)	0.6	(0.000)	0.8	(0.000)
CH_3CN (III)	0.7	(0.000)	14.7	(0.004)	46.8	(0.007)	3.4	(0.002)	5.4	(0.004)	4.5	(0.002)	4.0	(0.001)	8.3	(0.003)
CH_2Cl_2 (V)	12.7	(0.002)	9.8	(0.003)	8.8	(0.002)	18.4	(0.013)	18.4	(0.013)	21.7	(0.009)	17.2	(0.004)	18.7	(0.006)
Polar (VI)	48.9	(0.006)	22.6	(0.006)	27.0	(0.004)	26.0	(0.018)	43.6	(0.030)	34.7	(0.015)	30.8	(0.006)	37.3	(0.012)
Bound (VII)	37.7	(0.005)	50.4	(0.014)	12.7	(0.002)	51.3	(0.037)	30.4	(0.021)	38.5	(0.016)	45.6	(0.010)	33.9	(0.011)
Volatiles[2/]	--	--	1.0	(0.000)	--	--	--	--	--	--	--	--	1.8	(0.000)	1.0	(0.000)
TOTAL	100.0	(0.013)	100.0	(0.028)	100.0	(0.016)	100.0	(0.071)	100.0	(0.070)	100.0	(0.042)	100.0	(0.021)	100.0	(0.032)
^{14}C Recovery	106.8		87.5		120.2		94.9		96.8		87.9		92.6		98.3	

[1/] ppm (ug/g) FMC 57020 equivalent

[2/] KOH trap (see Section II.L)

TABLE 4

^{14}C RESIDUE DISTRIBUTION IN DIFFERENT FRACTIONS FROM RING-^{14}C FMC 57020 APPLICATION (2 lb/a)

	Corn						Oats				Sugar Beets				Cabbage	
	Silage		Stover		Grain		Straw		Grain		Tops		Beets			
Fraction	%	(ppm)	%	(ppm)	%	(ppm)	%	(ppm)	%	(ppm)	%	(ppm)	%	(ppm)	%	(ppm)
Hexane (IV)	--	--	--	--	--	--	0.6	(0.000)	--	--	1.0	(0.000)	--	--	0.4	(0.000)
CH_3CN (III)	--	--	3.8	(0.002)	6.7	(0.001)	6.5	(0.008)	12.3	(0.011)	18.6	(0.012)	3.4	(0.001)	3.2	(0.001)
CH_2Cl_2 (V)	21.2	(0.003)	14.0	(0.006)	26.1	(0.005)	15.0	(0.018)	31.0	(0.026)	23.0	(0.015)	22.2	(0.007)	21.9	(0.005)
Polar (VI)	35.2	(0.006)	18.9	(0.008)	50.3	(0.010)	20.1	(0.024)	25.2	(0.021)	21.2	(0.013)	23.9	(0.008)	49.9	(0.011)
Bound (VII)	43.6	(0.007)	63.3	(0.029)	16.9	(0.003)	57.8	(0.068)	31.5	(0.027)	36.2	(0.023)	50.5	(0.016)	24.6	(0.005)
TOTAL	100.0	(0.016)	100.0	(0.045)	100.0	(0.019)	100.0	(0.118)	100.0	(0.085)	100.0	(0.063)	100.0	(0.032)	100.0	(0.022)
^{14}C Recovery	83.8		98.1		103.5		83.4		96.5		87.8		94.5		98.1	

[1/] ppm (ug/g) FMC 57020 equivalent

Figure 1

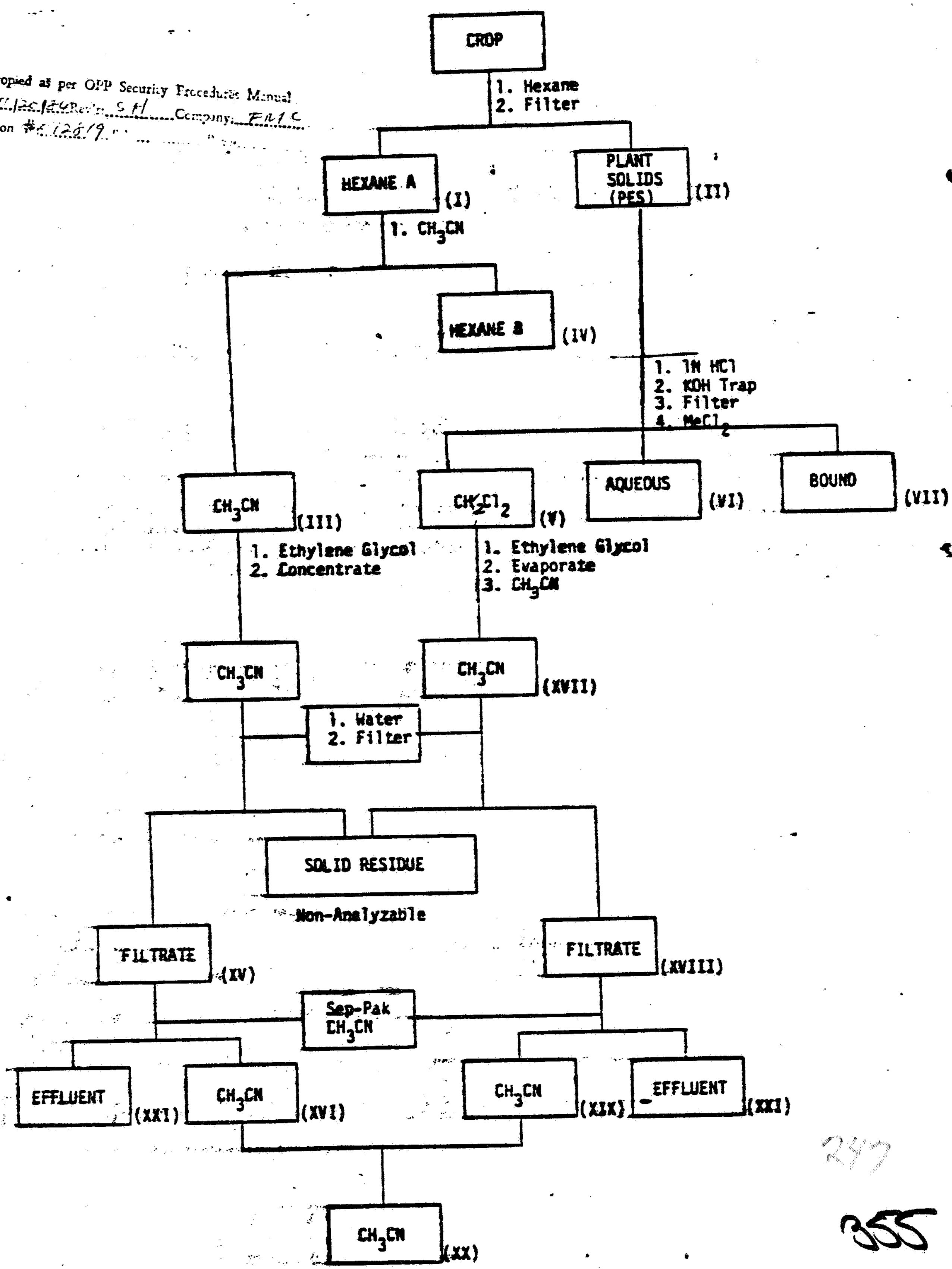
CROP
1. Hexane
2. Filter
HEXANE A (I)
PLANT SOLIDS (PES) (II)
1. CH3CN
HEXANE B (IV)
1. 1N HCl
2. KOH Trap
3. Filter
4. MeCl2
CH3CN (III)
CH2Cl2 (V)
AQUEOUS (VI)
BOUND (VII)
1. Ethylene Glycol
2. Concentrate
1. Ethylene Glycol
2. Evaporate
3. CH3CN
CH3CN
CH3CN (XVII)
1. Water
2. Filter
SOLID RESIDUE
Non-Analyzable
FILTRATE (XV)
FILTRATE (XVIII)
Sep-Pak
CH3CN
EFFLUENT (XXI)
CH3CN (XVI)
CH3CN (XIX)
EFFLUENT (XXI)
CH3CN (XX)

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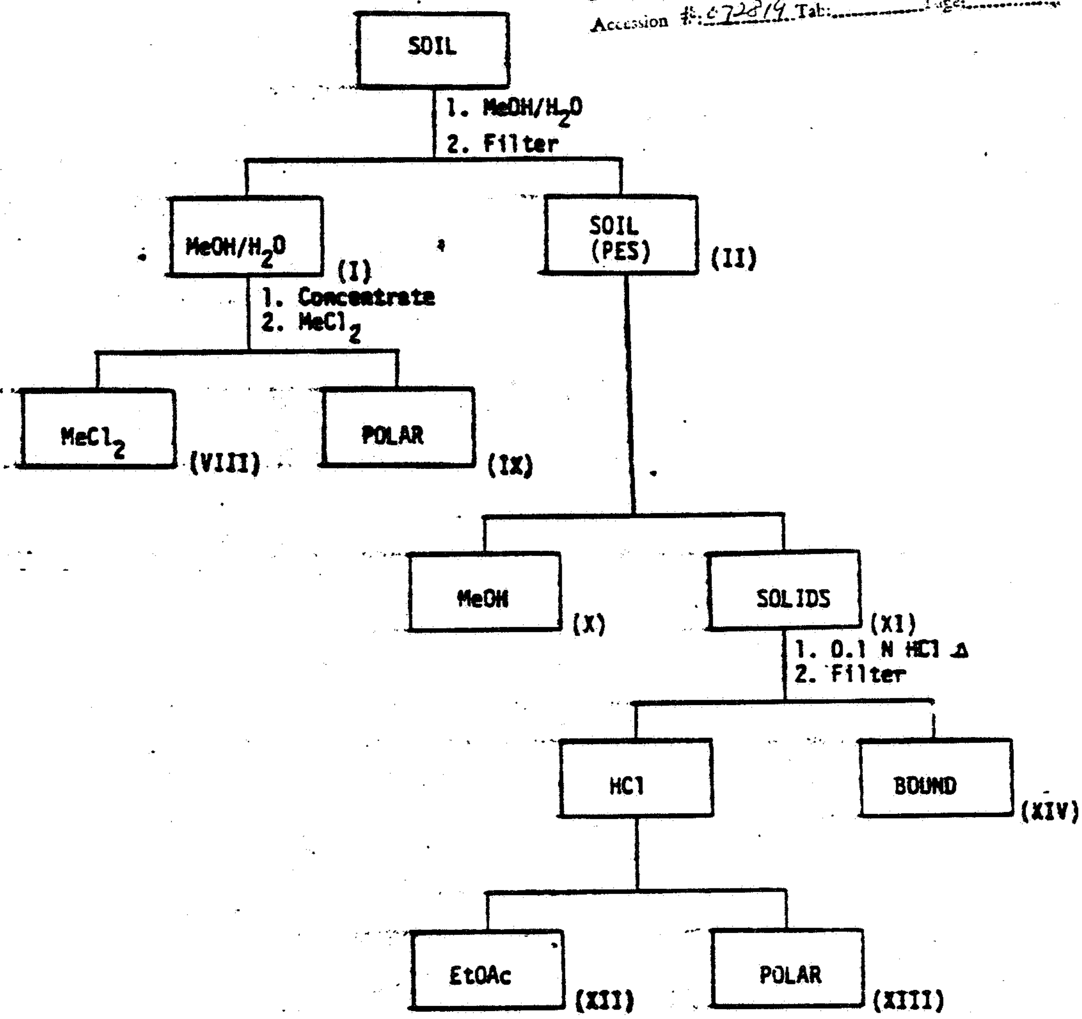
Figure 2


SOIL
1. MeOH/H2O
2. Filter
MeOH/H2O
(I)
1. Concentrate
2. MeCl2
SOIL (PES)
(II)
MeCl2
(VIII)
POLAR
(IX)
MeOH
(X)
SOLIDS
(XI)
1. 0.1 N HCl Δ
2. Filter
HCl
BOUND
(XIV)
EtOAc
(XII)
POLAR
(XIII)

Results from the HPLC and TLC analyses of acetonitrile fraction (XX) of sugar beet tops showed at least 11 metabolites and degradates from ring-labeled FMC 57020, the highest of which was 0.007 ppm (32 %) which was attributed to 2-chlorohydroxybenzyl alcohol (FMC 87015). O-chlorobenzyl alcohol amounted 0.004 ppm (24 %). Parent compound did not exceed 0.001 ppm (6 %). Other metabolites identified include monohydroxylated-FMC 57020 (FMC 77039 and FMC 60217), o-chlorobenzoic acid (FMC 14791), 2-chloro-5-hydroxybenzyl alcohol (FMC 87016).

HPLC and TLC analyses of the carbonyl ^{14}C organosoluble fraction showed the presence of at least 11 metabolites and degradates, the highest of which was 0.003 ppm. Most of the degradates were unknown and parent compound accounted for 0.001 ppm (table 5).

Table 5

HPLC PRODUCT DISTRIBUTION OF ^{14}C FMC 57020 RESIDUES IN SUGAR BEET TOPS

Ring-^{14}C FMC 57020				Carbonyl-^{14}C FMC 57020			
HPLC Fraction[1/]	%	ppm[2/]	Product	HPLC Fraction[1/]	%	ppm[2/]	Product
1-6	6.9	0.001	FMC 14791	1-7	7.0	0.001	Unknown
7-10	32.1	0.007	FMC 87015	8-13	41.7	0.003	Unknown
11-12	1.8	<0.001	FMC 87016	14-18	14.2	0.001	Unknown
13-16	6.1	0.001	FMC 83919	19-20	1.9	<0.001	Unknown
17-20	23.6	0.004	FMC 61569	21-23	3.6	<0.001	FMC 60217
21-22	2.8	<0.001	FMC 60217	24-26	2.5	<0.001	FMC 77039
23-25	3.9	0.001	FMC 77039	27-30	5.5	<0.001	Unknown
26-29	5.7	0.001	Unknown	31-32	3.0	<0.001	Unknown
30-34	5.7	0.001	Unknown	33-38	9.7	0.001	FMC 57020
35-39	5.7	0.001	FMC 57020	39-42	6.1	0.001	Unknown
40-45	5.7	0.001	Unknown	43-45	4.8	<0.001	Unknown
TOTAL	100.0	0.018		TOTAL	100.0	0.007	
HPLC Recovery	88.0			HPLC Recovery	101.7		

1/ Retention times for the various fractions are shown in Appendix B

2/ ppm (µg/g) FMC 57020 equivalent (see Appendix D)

Results from the HPLC and TLC analyses of organosoluble residues from oat straw are shown in table 6. At least 12 metabolites were found in the extracts from the ring-labeled test and a monohydroxylated FMC 57020 was the highest (0.006 ppm, 23.2%). Analysis of ^{14}C-carbonyl organosoluble fractions showed the presence of at least 12 metabolites, the highest of which was 0.003 ppm due to FMC 65317. In both lables, FMC 57020 accounted for 0.002 ppm (ca. 9%).

Table 6

HPLC PRODUCT DISTRIBUTION OF ^{14}C FMC 57020 RESIDUES IN OAT STRAW

Ring-^{14}C FMC 57020				Carbonyl-^{14}C FMC 57020			
HPLC Fraction[1/]	%	ppm[2/]	Product	HPLC Fraction[1/]	%	ppm[2/]	Product
1-6	10.2	0.002	FMC 14791	1-6	3.9	<0.001	Unknown
7-9	7.0	0.002	FMC 87015	7-9	1.0	<0.001	Unknown
10-12	5.8	0.001	FMC 87016	10-12	4.5	<0.001	Unknown
13-16	17.3	0.004	FMC 83918	13-17	8.6	0.001	FMC 83918
17-18	4.5	0.001	Unknown	18-20	33.4	0.003	FMC 65317
19-20	3.3	0.001	FMC 65317	21-23	9.6	0.001	FMC 60217
21-23	6.1	0.001	FMC 60217	24-26	6.2	0.001	FMC 77039
24-26	23.2	0.006	FMC 77039	27-29	3.8	<0.001	Unknown
27-31	4.5	0.001	Unknown	30-35	4.5	<0.001	Unknown
32-38	5.4	0.001	Unknown	36-38	1.1	<0.001	Uknown
39-40	8.8	0.002	FMC 57020	39-40	20.6	0.002	FMC 57020
41-45	3.9	0.001	Unknown	41-45	2.8	<0.001	Unknown
TOTAL	100.0	0.023		TOTAL	100.0	0.008	
HPLC Recovery	96.8			HPLC Recovery	99.0		

1/ Retention times for the various fractions are shown in Appendix B

2/ ppm (µg/g) FMC 57020 equivalent (see Appendix E)

Results from the ^{14}C residue analysis on soil cores taken at 0 time, 4, 10 and 16 months after chemical application are shown in table 7 and 8.

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Table 7

TOTAL ^{14}C RESIDUES IN SOIL 1/

Depth	Carbonyl-^{14}C FMC 57020				Ring-^{14}C FMC 57020			
	Zero	4 Mo	10 Mo	16 Mo	Zero	4 Mo	10 Mo	16 Mo
0-6"	1.081	0.404	0.531	0.147	0.896	0.373	0.330	0.182
6-12"	0.086	0.190	0.065	0.012	0.029	0.389	0.088	0.012

1/ ppm (µg/g equivalent to FMC 57020) calculated by summation of ^{14}C in MeOH:H_2O blend and combustion analysis of PES (II) (Figure 3)

Table 8

TOTAL PPM (µg/g) OF FMC 57020 IN SOIL

Depth (Inches)	Carbonyl-^{14}C FMC 57020				Ring-^{14}C FMC 57020			
	Zero	4 Mo	10 Mo	16 Mo	Zero	4 Mo	10 Mo	16 Mo
0-6	1.001	0.245	0.280	0.028	0.834	0.211	0.178	0.034
6-12	0.069	0.138	0.027	1/	0.020	0.244	0.036	1/

1/ No identification work was done on the organosoluble fraction due to the low level of ^{14}C residue (0.002 ppm)

The four month sampling showed an increase in ^{14}C residues in the 6-12" layer indicating that the residues leached into the lower soil profile. After 16 months, the 6-12" layer contained low levels (0.01 ppm) of ^{14}C residues. This may indicate the residues leached further to soil layers deeper than 12 inches.

The major product detected in soil at all sampling intervals was FMC 57020. FMC 65317, an anaerobic soil metabolite was detected in older samples (10 and 16 months) but at levels lower than 1.0% (0.004 ppm) of the total soil residues. Polar products generally increased with time. Bound residues also increased with time and accounted for 65-95% of the total ^{14}C residues at 16 months (tables 9-12).

Conclusion

The application of FMC 57020 at the rate of 2 lb ai/a (1.6-1.7x of maximum use rate) resulted in residue accumulation in rotational crops (corn, oats, cabbage and sugar beet) planted 10 months after chemical application. However, residue analysis showed that a majority of these residues were either plant tissue bound or polar. Organosoluble residues accounted for less than 0.02 ppm.

Results from the soil analyses indicate FMC 57020 has a potential to leach. 257

The data support a 10 month rotational crop interval for FMC 57020 when used at 2 lb ai/A/yr or less.

TABLE 9

CARBONYL-^{14}C FMC 57020 MATERIAL BALANCE/PRODUCT DISTRIBUTION IN 0-6" SOIL CORE

	0 Day		4 Months		10 Months			16 Months		
	% Dist.	% FMC 57020	% Dist.	% FMC 57020	% Dist.	% FMC 57020	% FMC 65317	% Dist.	% FMC 57020	% FMC 65317
$MeCl_2$ (VIII)	93.0	92.6	62.3	60.7	40.1	39.7	-	6.4	5.8	-
MeOH (X)	-	-	-	-	13.7	8.6	0.1	12.0	8.9	0.2
EtOAc (XII)	-	-	-	-	7.8	4.5	0.4	8.5	4.4	0.4
TOTAL FMC 57020	-	92.6	-	60.7	-	52.8	-	-	19.1	-
TOTAL FMC 65317	-	-	-	-	-	-	0.5	-	-	0.6
UNIDENTIFIED PRODUCTS[1/]	-	0.4	-	1.6	-	8.3	-	-	7.2	-
TOTAL ORGANOSOLUBLES	93.0	-	62.3	-	61.6	-	-	26.9	-	-
POLAR AQUEOUS (IX, XIII)	0.1	-	0.9	-	7.4	-	-	7.6	-	-
BOUND RESIDUE (XIV)	6.9	-	36.8	-	31.0	-	-	65.5	-	-
TOTAL	100.0		100.0		100.0			100.0		

[1/] Unidentified products (8), none exceeding 1.6%

TABLE 10

CARBONYL-^{14}C FMC 57020 MATERIAL BALANCE/PRODUCT DISTRIBUTION IN 6-12" SOIL CORE

	0 Day		4 Months		10 Months			16 Months[2/]		
	% Dist.	% FMC 57020	% Dist.	% FMC 57020	% Dist.	% FMC 57020	% FMC 65317	% Dist.	% FMC 57020	% FMC 65317
$MeCl_2$ (VIII)	80.9	80.3	73.9	72.7	31.6	31.2	-	4.6	-	-
MeOH (X)	-	-	-	-	19.1	10.1	-	13.6	-	-
EtOAc (XII)	-	-	-	-	-	-	-	-	-	-
TOTAL FMC 57020	-	80.3	-	72.7	-	41.3	-	-	-	-
TOTAL FMC 65317	-	-	-	-	-	-	-	-	-	-
UNIDENTIFIED PRODUCTS[1/]	-	0.6	-	1.2	-	9.4	-	-	-	-
TOTAL ORGANOSOLUBLES	80.9	-	73.9	-	50.7	-	-	18.2	-	-
POLAR AQUEOUS (IX, XIII)	-	-	0.5	-	0.8	-	-	0.8	-	-
BOUND RESIDUE (II OR XIV)	19.1	-	25.6	-	48.5	-	-	81.0	-	-
TOTAL	100.0		100.0		100.0			100.0		

[1/] Unidentified products (8), none exceeding 6.6%

[2/] No identification work was done on the organosoluble fractions due to the low level of ^{14}C residue (0.002 ppm)

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- 2D

TABLE 11

RING-^{14}C FMC 57020 MATERIAL BALANCE/PRODUCT DISTRIBUTION IN 0-6" SOIL CORE

	0 Day		4 Months		10 Months			16 Months		
	% Dist.	% FMC 57020	% Dist.	% FMC 57020	% Dist.	% FMC 57020	% FMC 65317	% Dist.	% FMC 57020	% FMC 65317
$MeCl_2$ (VIII)	93.5	93.1	57.8	56.6	39.7	39.2	-	8.6	7.8	-
MeOH (X)	-	-	-	-	14.7	10.3	0.4	9.0	7.2	0.2
EtOAC (XII)	-	-	-	-	5.8	4.6	0.4	6.0	4.0	0.3
TOTAL FMC 57020	-	93.1	-	56.6	-	54.1	-	-	19.0	-
TOTAL FMC 65317	-	-	-	-	-	-	0.8	-	-	0.5
UNIDENTIFIED PRODUCTS[1/]	-	0.4	-	1.2	-	5.3	-	-	4.1	-
TOTAL ORGANOSOLUBLES	93.5	-	57.8	-	60.2	-	-	23.6	-	-
POLAR AQUEOUS (IX, XIII)	1.0	-	2.0	-	4.8	-	-	7.2	-	-
BOUND RESIDUE (II or XIV)	5.5	-	40.2	-	35.0	-	-	69.2	-	-
TOTAL	100.0		100.0		100.0			100.0		

[1/] Unidentified products (8), none exceeding 0.5%

TABLE 12

RING-^{14}C FMC 57020 MATERIAL BALANCE/PRODUCT DISTRIBUTION IN 6-12" SOIL CORE

	0 Day		4 Months		10 Months			16 Months		
	% Dist.	% FMC 57020	% Dist.	% FMC 57020	% Dist.	% FMC 57020	% FMC 65317	% Dist.	% FMC 57020	% FMC 65317
$MeCl_2$ (VIII)	73.1	72.0	63.8	62.6	32.1	31.5	-	4.7	-	-
MeOH (X)	-	-	-	-	16.1	9.8	0.7	0.0	-	-
EtOAc (XII)	-	-	-	-	-	-	-	-	-	-
TOTAL FMC 57020	-	72.0	-	62.6	-	41.3	-	-	-	-
TOTAL FMC 65317	-	-	-	-	-	-	0.7	-	-	-
UNIDENTIFIED PRODUCTS[1/]	-	1.1	-	1.2	-	6.2	-	-	-	-
TOTAL ORGANOSOLUBLES	73.1	-	63.8	-	48.2	-	-	4.7	-	-
POLAR AQUEOUS (IX, XII)	0.9	-	2.6	-	0.7	-	-	0.6	-	-
BOUND RESIDUE (II or XIV)	26.0	-	33.6	-	51.1	-	-	94.7	-	-
TOTAL	100.0		100.0		100.0			100.0		

[1/] Unidentified products (8), none exceeding 1.8%
[2/] No identification work was done on the organosoluble fraction due to low level ^{14}C residue (<0.001 ppm)

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3.16 Uptake, Depuration and Bioconcentration of ^{14}C FMC 57020 by Bluegill Sunfish. W.A. McAllister and L. Franklin, Analytical Bio-Chemistry Laboratories, Inc. for FMC Corp., PC-0018, May 21, 1984, EPA Acc. No. 072819 (Rf. 16).

Experimental

Bluegill sunfish (Wt. 3.4 $\pm$ .096 g, Length 48 $\pm$ 3.4 cm) were exposed to methylene ^{14}C FMC 57020 at a nominal concentration of 0.02 mg/l under a flow-through condition for 28 days.

A proportional diluter system was used for the intermittent introduction of ^{14}C FMC 57020 and diluent water into the 100 L test aquaria (70 L of water) at an average flow rate of about 333 ml/min/aquarium (6.9 times/24 hr).

Methylene-^{14}C FMC 57020 aqueous solution (with 0.75% N,N-dimethylformamide; DMF)(0.042 mg/ml, 1.78×10^4 dpm/ug) was used by the diluter toxicant injection system.

One hundred and thirty fish each were introduced into the test aquarium and a control aquarium. After 28 days of exposure, the water (70 l) in each test aquarium was replaced by uncontaminated water.

Water and fish were sampled throughout the uptake and depuration (14 days) period following the schedule outlined in table 1. The number of fish sampled and the amount of water sampled are also shown in table 1.

Radioassay of water samples was done using LSC. For each sampling effort, three fish were divided into two portions, fillet (edible) and viscera (non-edible) portions and pooled. Two additional fish from each test chamber were pooled into control and treated samples for whole fish analysis. The individual samples were homegenized with dry ice, weighed and subjected to combustion analysis.

For the metabolite characterization, 18 fish from each aquarium were sampled and pooled into control and treated groups. Eleven of these fish from each group were divided into edible and non-edible portions and 7 were used for whole fish analysis.

The fish tissue extractability was determined by mixing 5 g of each fish tissue with a magnetic stirrer in 20 ul of hexane or methanol for three times. The combined filtrate volumes were adjusted and radioassayed.

Results

The measured ^{14}C radioactivity calculated as FMC 57020 in test water and fish tissue during 28 days exposure and 14 days depuration is shown in table 2. The average water concentration during uptake phase was 0.24 ($\pm$ 0.0021) mg/l. After day 1 of

TABLE 1-: Sampling schedule[a] for radioanalyses, metabolite characterization and water quality determinations during the bioconcentration study with bluegill sunfish exposed to ^{14}C-FMC 57020.

	Uptake Phase (Day)								Depuration Phase (Day)				
	0	1	3	7	10	14	21	28	1	3	7	10	14
Fish													
Day sampled		X	X	X	X	X	X	X	X	X	X	X	X
Number of fish sampled including metabolite study fish	5	5	5	5	5	25	25	30	5	5	5	5	5
Number of fish used for fillet and viscera samples and extra fish for metabolite study	3	3	3	3	3	18	18	20	3	3	3	3	3
Number of fish used for whole fish analyses	2	2	2	2	2	7	7	10	2	2	2	2	2
Total fish remaining after sampling including metabolite study fish	130	125	120	115	110	105	80	55	25	20	15	10	5
Total residue analysis of fillet, viscera and whole fish		X	X	X	X	X	X	X	X	X	X	X	X
Metabolite characterization samples						X	X	X					
Extractability of fillet, viscera and whole fish tissues								X					
Water													
Day sampled	X	X	X	X	X	X	X	X	X	X	X	X	X
Total amount sampled (mls)	1000	250	250	250	250	1000	1000	1000	250	250	250	250	250
Total residue analysis	X	X	X	X	X	X	X	X	X	X	X	X	X
Water quality measurements	X	X	X	X	X	X	X	X	X	X	X	X	X

[a]This schedule is also applicable to the control samples.

depuration phase, no quantifiable levels (<0.00014 mg/l) of radioactivity were found in the water.

The data suggest that the compound ceased accumulating (on the whole fish basis) after 1 day of exposure. The tissue residues after 28 days of exposure were 0.97 ppm for whole fish, 0.24 ppm for fillet and 1.8 ppm for viscera with corresponding bioconcentration factors of 40X, 10X, and 75X (table 2).

Ninety-four to 97% of the accumulated residues were eliminated in three days and at the end of the depuration period, 99, 97 and 99% were eliminated from whole fish, fillet and viscera, respectively (table 3).

The results of the extractability experiments are shown in table 4.

No mortality was observed in any test chamber during the study.

Comments

Methylene-^{14}C FMC 57020 was used in this study, so aromatic portion of the compound could not be well monitored. If ring-labeled FMC 57020 is used in a fish accumulation study, will the results be more or less the same as in this study?

Conclusion

This study was very well done. FMC 57020 has a moderate tendency to bioaccumulate in bluegill sunfish with a bioaccumulation factor of 40X for whole fish, but depuration occurs rapidly to low but measurable levels upon removal of the fish to uncontaminated environment.

This study can be acceptable depending on the adequate explanation regarding the labeling position (see comments).

3.17 Analysis of FMC 57020 Residues in Bluegill Sunfish and Water, T.A. Bixler, FMC Corp. p-0889, 6/5/84. Rf E3623, EPA Acc. No. 072819 (Rf. 17).

Experimental

Fish and water samples taken in the bioaccumulation study (see section 3.15) were analyzed for metabolite identification.

The following unlabeled standards were used as HPLC reference standards.

TABLE 2. Measured ^{14}C-radioactivity calculated as FMC 57020 in test water and fish tissue during 28 days exposure and 14 days depuration with bluegill sunfish.

		Concentration of ^{14}C-FMC 57020					
	Water[c]	Fillet		Whole Fish		Viscera	
Day	mg/l	ppm	BCF[a]	ppm	BCF[a]	ppm	BCF[a]
Uptake 0	0.022[d]	<0.0029[e]		<0.0027[e]		<0.0029[e]	
1	0.021	0.23	10X	0.80	36X	1.3	59X
3	0.024	0.30	14X	0.81	37X	2.3	105X
7	0.026	0.36	16X	0.74	32X	1.7	74X
10	0.024	0.23	10X	0.83	36X	1.7	74X
14	0.027	0.25	10X	0.64	27X	1.5	62X
21	0.024	0.21	8.8X	0.75	31X	1.3	54X
28	0.026	0.24	10X	0.97	40X	1.8	75X
Depuration 1	0.00019	0.029		0.33		0.46	
3	<0.00014[b]	0.015		0.052		0.054	
7	<0.00016	0.0085		0.020		0.030	
10	<0.00014[b]	0.0057		0.015		0.020	
14	<0.00014[b]	0.0066		0.0090		0.014	

[a]Daily bioconcentration factor obtained by dividing the tissue concentration by the mean measured water concentration up to and including the respective sampling day.

[b]Below minimum quantifiable limits (see page 8 of text). Water MQL = 0.00015 mg/l, whole fish MQL = 0.0031 mg/l, fillet MQL = 0.0030 mg/l and viscera MQL = 0.0031 mg/l.

[c]All values have been rounded to represent two significant figures.

[d]Samples taken immediately prior to addition of fish.

[e]Samples taken from acclimation chamber immediately prior to separation for treatment with ^{14}C-FMC 57020.

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TABLE 3: Depuration of ^{14}C as FMC 57020 from bluegill sunfish during a 14-day clearance period.

	Whole Fish[b]		Fillet[b]		Viscera[b]	
Depuration	Depuration Concentration (ppm)	Percent Depuration	Depuration Concentration (ppm)	Percent Depuration	Depuration Concentration (ppm)	Percent Depuration
1	0.33	66	0.029	88	0.46	74
3	0.052	95	0.015	94	0.054	97
7	0.020	98	0.0085	96	0.030	98
10	0.015	98	0.0057	98	0.020	99
14	0.0090	99	0.0066	97	0.014	99

[a]Depuration rates are expressed as a percentage of the day 28 ^{14}C-FMC 57020 concentrations of 0.97 ppm for whole fish, 0.24 ppm for fillet, and 1.8 ppm for viscera.

[b]All values have been rounded to two significant figures.

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TABLE 4: Extractability of ^{14}C, as FMC 57020, from bluegill sunfish tissue after 28 days of exposure.

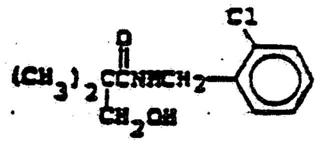
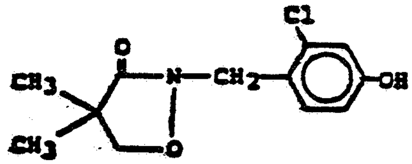
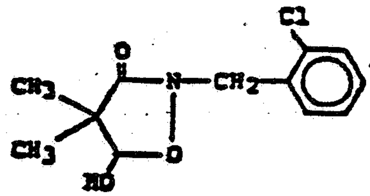
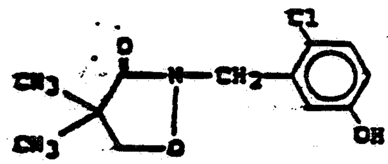
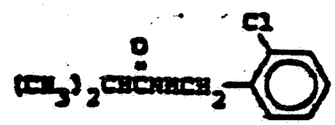
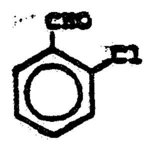
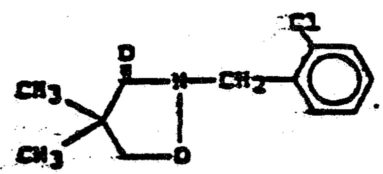
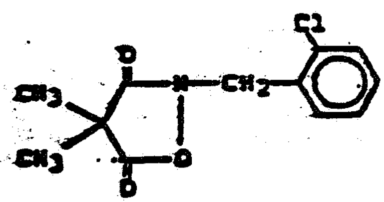
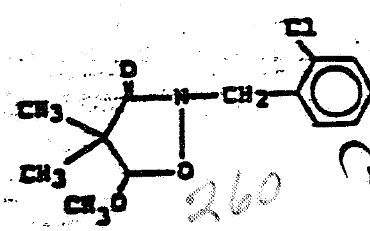
Hexane Extraction

	Pre-Extracted Tissue (ppm)	Extract (ppm)[a]	% in Extract	Post-Extracted Tissues (ppm)[a]	% in Post-Extracted Tissues	Total % Accounted
Fillet	0.24	0.17	71%	0.051	21%	92%
Whole Fish	0.97	0.36	37%	0.50	52%	89%
Viscera	1.8	0.57	32%	0.91	51%	83%

MeOH Extraction

	Pre-Extracted Tissue (ppm)	Extract (ppm)[a]	% in Extract	Post-Extracted Tissues (ppm)[a]	% in Post-Extracted Tissues	Total % Accounted
Fillet	0.24	0.24	100%	0.0057	2.4%	102%
Whole Fish	0.97	0.91	94%	0.021	2.2%	96%
Viscera	1.8	1.5	83%	0.055	3.1%	86%

[a]Values adjusted to reflect pre-extracted tissue ppm equivalents.

	FMC Number	Name	Structure
A)	FMC 65317	N-[(2'-Chlorophenyl)methyl]-3-hydroxy-2,2-dimethyl propanamide	
B)	FMC 62667	2-[(2'-Chloro-4'-hydroxyphenyl)methyl]-4,4-dimethyl-3-isoxazolidinone	
C)	FMC 60217	2-[(2'-Chlorophenyl)methyl]-4,4-dimethyl-5-hydroxy-3-isoxazolidinone	
D)	FMC 77039	2-[(2'-Chloro-5'-hydroxyphenyl)methyl]-4,4-dimethyl-3-isoxazolidinone	
E)	FMC 55667	N-[(2'-Chlorophenyl)methyl]-2-methyl propanamide	
F)	FMC 14788	2-Chlorobenzaldehyde	
G)	FMC 57020	2-[(2'-Chlorophenyl)methyl]-4,4-dimethyl-3-isoxazolidinone	
H)	FMC 55626	2-[(2'-Chlorophenyl)methyl]-4,4-dimethyl-5-oxo-3-isoxazolidinone	
I)	FMC 57061	2-[(2'-Chlorophenyl)methyl]-4,4-dimethyl-5-methoxy-3-isoxazolidinone	

Control fish water (ca. 800 ml) was fortified at 0.025 mg/l (400,000 dpm) with methylene-^{14}C FMC 57020. About 10g of NaCl were added to the water prior to fortification. The water was passed through two activated C-18 Sep-Pak® columns (methanol 10 ml, water 2x20ml). The Sep-paks were eluted with CH_2Cl_2 (2 x 20 ml). The CH_2Cl_2 was dried over anhydrous Na_2SO_4 and used for HPLC analysis.

Control fish (fillet and viscera, 20g each) were fortified at 0.25 ug/g (ca. 89,000 dpm) and 15 ug/g (ca. 550,000 dpm) respectively with methylene ^{14}C FMC 57020. Each sample was blended with methanol for 5 minutes and then filtered. The methanol filtrate was concentrated and taken up in hexane. The hexane was partitioned in acetonitrile. The acetonitrile was concentrated and applied to an 8 g Bio-Bead® SX-3 column and eluted with cyclohexane : Methyl chloride = 85 : 15.

The extraction procedure for samples from the bioaccumulation study is the same as described for fortified control samples and is shown in figures 1 and 2.

Results

Extraction of the fortified control fish water and subsequent purification and HPLC analysis showed >95% was parent compound. For the fortified fish samples, >98% of parent compound was recovered and 90% of fish oil was removed by the purification process in Bio-Bead column.

The material balance of 0 time and 28 day fish water treated with methylene ^{14}C FMC 57020 is shown in table 1.

TABLE 1

METHYLENE-^{14}C FMC 57020 FISH WATER

MATERIAL BALANCE[1/]/PRODUCT DISTRIBUTION

	0 Day		28 Day	
Fraction	% Dist.	µg/g	% Dist.	µg/g
FMC 57020	95.7	0.021	93.3	0.024
Unidentified[2/]	1.3		2.3	
$MeCl_2$ (I)	97.0		95.6	
Aqueous (II)	3.0		4.4	
Total	100.0	0.022[3/]	100.0	0.026[3/]

1/ Normalized percent distribution-recoveries of 92.2% (0 day) and 93.6% (28 day) based on data from A1.

2/ Unidentified products (2), neither exceeding 1.4% of total residue

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FIGURE 1

EXTRACTION SCHEME FOR FISH WATER

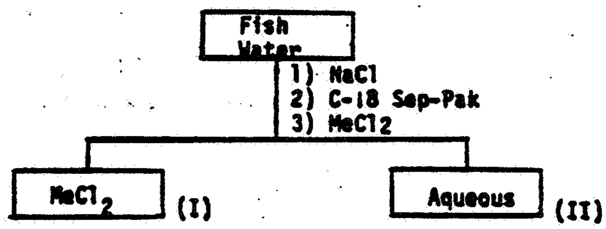
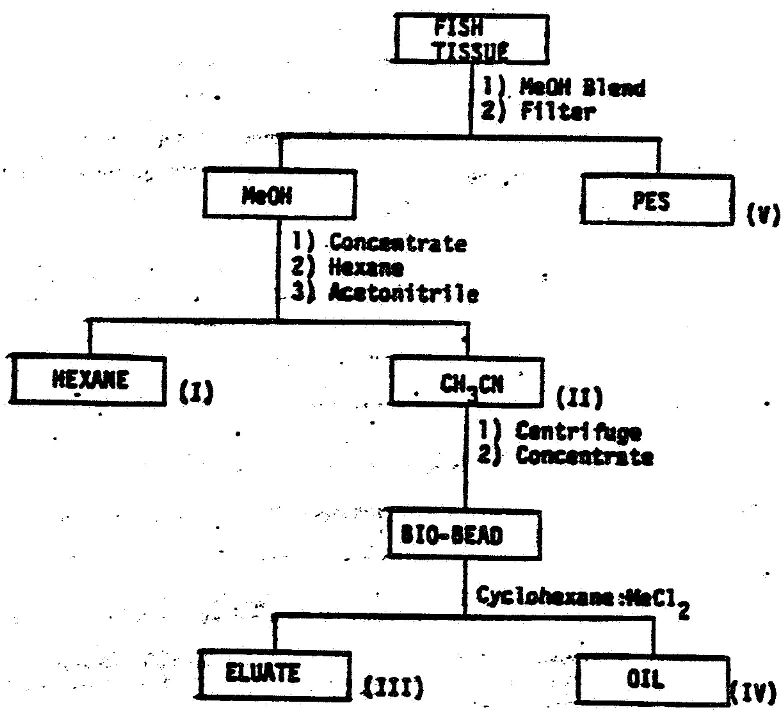


FIGURE 2

EXTRACTION SCHEME FOR FISH TISSUE



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The HPLC analyses showed that FMC 57020 was stable throughout the study.

The results from the fillet and viscera samples are summarized in table 2. The major detectable product at each intervals in both fillet and viscera samples was FMC 57020.

Table 2

METHYLENE-^{14}C FMC 57020 FISH TISSUE
MATERIAL BALANCE[1/]/PRODUCT DISTRIBUTION

Product	Fillet				Viscera			
	14 Day		28 Day		14 Day		28 Day	
	%	µg/g[2/]	%	µg/g[2/]	%	µg/g[2/]	%	µg/g[2/]
FMC 65317	3.2	0.008	4.1	0.01	1.0	0.015	2.0	0.036
FMC 62667	-	-	-	-	1.4	0.021	1.8	0.032
FMC 60217	0.8	0.002	1.3	0.003	0.8	0.012	1.3	0.023
FMC 77039	-	-	1.3	0.003	0.6	0.009	0.6	0.011
FMC 55657	0.7	0.002	2.6	0.006	1.0	0.015	1.2	0.022
FMC 14788	1.2	0.003	1.8	0.004	2.0	0.03	8.6	0.155
FMC 57020	58.9	0.147	53.1	0.127	41.6	0.624	28.0	0.504
FMC 55626	2.6	0.007	1.3	0.003	7.2	0.108	6.7	0.121
FMC 57061	-	-	-	-	0.9	0.031	0.6	0.011
Unidentified[3/]	15.5		8.0		7.9		7.1	
Eluate (III)	82.9		73.5		64.4		57.9	
Oil (IV)	10.1		18.2		18.4		30.8	
Hexane (I)	5.1		2.4		13.4		7.0	
PES (V)	1.9		5.9		3.8		4.3	
Total	100.0	0.25[4/]	100.0	0.24[4/]	100.0	1.5[4/]	100.0	1.8[4/]

1/ Normalized percent distribution. Recoveries based on total ^{14}C-residue from A1., ranged from 73.8% - 100.5%

2/ µg/g values equivalent to parent compound

3/ Unidentified products (7), none exceeding 4.2% of total ^{14}C- residue

4/ Total ^{14}C residues (µg/g FMC 57020 equivalents) of each sample as reported in A1

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FMC 57020 appears to be metabolized by a variety of processes including oxidation, hydroxylation, heterocyclic ring opening, methylation and decarboxylation. The presence of small levels of ^{14}C, 2-5% in fillet and 7-13% in viscera, as hexane soluble radiocarbons suggests some incorporation into fats and/or oils. Additional amounts of radiocarbon (10-30%) which co-elutes by gel permeation chromatography with residual fish oil may be attributed to higher molecular weight lipophilic and/or polar metabolite conjugates.

Conclusion

Metabolite analysis of accumulated radiocarbon after exposure of bluegill sunfish to methylene-^{14}C FMC 57020 showed that more than 50% in fillet and about 30-40% in viscera was attributed to parent compound. Nine minor degradation products, none exceeding 9% of the total ^{14}C residues, were observed. There were indications that the radiocarbon was incorporated into fats/oils and higher molecular weight lipophillic/ polar metabolite conjugates.

4.0 EXECUTIVE SUMMARY

4.1 Hydrolysis

Data were reviewed in a previous evaluation (12/3/82). FMC 57020 is stable to hydrolysis over the pH range of 4.64 to 9.25 at the temperature of 25°C $\pm$ 0.5°C. This requirement is satisfied.

4.2 Aqueous Photolysis

FMC 57020 appears to undergo photodegradation to give 2-Chlorobenzoic acid as a major product and many other degradates with a half-life about 87 days under natural sunlight. 2-Chlorobenzoic acid appears to be degraded further.

This study is not acceptable (as explained in section 3.1 above) because half-lives were not derived in a consistent manner and actual recoveries were not reported.

4.3 Soil photolysis

This study is not acceptable (as explained in section 3.2 above) because:

- o organovolatiles were not trapped (material balance was poor),
- o soil was not sterilized,
- o the temperature of soil was not monitored,
- o degradation rate was not reported,
- o identification of degradation products was not done,
- o the Mylar film may have excluded those wavelengths that could cause photodegradation.

4.4 Aerobic Soil Metabolism

Three (3) studies submitted and reviewed in sections 3.3, 3.5 and 3.6. The study in section 3.3 was not acceptable, but the studies in sections 3.5 and 3.6 in combination satisfy the aerobic soil metabolism data requirement.

FMC 57020 is mineralized in soil under aerobic conditions. CO_2 evolution and soil binding increase with time. The rate and the degree of mineralization and soil binding vary with soil types. Both rings of the molecule are susceptible to the mineralization process. Unchanged FMC 57020 is the primary residue in soil, and polar/non-polar metabolites are minor residues. The estimated half-lives varied from 56 to 173 days depending on soil type.

The aerobic soil metabolism data requirement is satisfied.

4.5 Anaerobic Soil Metabolism

FMC 57020 readily degrades to FMC 65317 as a major product under anaerobic conditions. Another 12 minor degradation products were detected. No CO_2 evolution was observed. Data indicate that FMC 65317 persists under anaerobic conditions.

The anaerobic soil metabolism data requirement is satisfied.

4.6 Laboratory Leaching

FMC 57020 appears to have a low to intermediate mobility in Cosad sandy loam, Dunkirk silt loam and Hagerstown clay loam but a high mobility in Leon fine sand, which indicates a potential for leaching in sandy soils. FMC 65317, an anaerobic soil degradate of FMC 57020, has a very high mobility in all soil types.

Adsorption/desorption constants of FMC 57020 in the above soil types indicate that FMC 57020 has a high leaching potential.

4.7 PESTANS Modeling

Although computer modeling is not required, the correct version of PESTANS should be obtained. As well, PRZM should be used in addition to or in place of PESTANS, if possible.

4.8 Field Leaching

FMC 57020 appears to have low mobility potential under actual field conditions (loamy sand, 2.0 lb ai/a, 13.9 inches of water) since no detectable levels of the compound or its metabolites were found in soil samples taken deeper than 1 foot (see section 3.11). However, the following 5 questions need to be addressed before the field leaching potential can be determined:

- o Do FMC 57020 and FMC 65317 form respective salts with HCl?
- o If they do not form salts, are they soluble enough to be extracted efficiently in water?
- o If they form salts, isn't it necessary to basify the acid extracts before partitioning in an organic solvent?
- o It was reported that the method sensitivity for FMC 57020 and FMC 65317 in soil was validated to 0.10 ppm and that the detection limit was 0.02 ppm for both compounds. However, none of the residue levels were between 0.02 and 0.10 ppm.

Also, results from the rotational crop study show leaching below 12 inches could have occurred (see section 3.14). These issues must be resolved before field leaching potential can be determined.

4.9 Field Dissipation Study

FMC 57020 residue levels in top 6 inches and 6-12 inches after application of the compound at 2.0 lb ai/a to four sites declined with time. The half-lives need to be re-estimated by the registrant (see comments in section 3.13).

4.10 Rotational Crops

The application of ^{14}C-FMC 57020 at the rate of 2 lb ai/a (1.6-1.7x maximum label rate) results in low residues in rotational crops (corn, oats, cabbage and sugar beet) planted 10 months after chemical application. A majority of these residues are either plant tissue bound or polar. Organosolubles account for less than 0.02 ppm. Residue levels were higher in the mature rotational crops as compared to the immature ones. Total ^{14}C did not exceed 0.063 ppm in corn, cabbage or sugar beets, but reached a maximum of 0.118 ppm in mature oat straw. The data support a 10 month rotational crop interval.

The rotational crop study data requirement is satisfied. Additional data will be needed if a shorter interval is desired.

4.11 Fish accumulation

FMC 57020 has a moderate tendency to bioaccumulate in bluegill sunfish under flow-through conditions. A bio-accumulation factor of 40x for whole fish was found, but depuration occurs rapidly to low but measurable levels upon removal of the fish to uncontaminated water. FMC 57020 appears to be metabolized in the fish by a variety of processes including oxidation, hydroxylation, heterocyclic ring opening, methylation, and decarboxylation. There are indications that the methylene carbon is incorporated into fats/oils and higher molecular weight lipophillic/polar metabolite conjugates.

The fish accumulation data requirement is satisfied under the condition that the registrant provides an adequate explanation about the comment in section 3.16.

5.0 CONCLUSION/RECOMMENDATION

5.1 The following environmental data requirements are satisfied for the registration of Command:

- o hydrolysis (EAB review dated 12/3/82)
- o aerobic soil metabolism
- o anaerobic soil metabolism
- o laboratory leaching/aged leaching
- o rotational crops

5.2 The following environmental data requirements on Command are not satisfied:

- o aqueous photolysis (see section 4.1)
- o fish accumulation (see section 4.9)
- o field dissipation (see section 4.7)
- o soil photolysis (see section 4.3)

5.3 The correct version of PESTANS modeling or if possible, PRZM modeling may be done for leaching potential. Note that such data are not required for registration.

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November 21, 1984
Environmental Chemistry Review Section #1
Exposure Assessment Branch/HED

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