114501

TO: EEB
Mr. Bushong

DATE: 3/27/79

To: PRODUCT MANAGER Sanders (12)
TS-767

Through: Dr. Gunter Zweig, Chief

From: Review Section No. 1
Environmental Fate Branch

Attached please find the environmental fate review of:

Reg./File No.: 1016-EUP-LE, 962152

Chemical: Dimethyl N,N'-[thiobis[(methylimino)carbonyloxy]] bis[ethanimidothioate] (UC51762)

Type Product: Insecticide

Product Name: Larvin 50 Insecticide

Company Name: Union Carbide Corporation

Submission Purpose: use on cotton and soybeans

Date In: 12/18/78

Date Out: 3/27/79

1. Introduction

1.1 This is the first data submission in support of an applicaton for a 2-year Experimental Use Permit for use of LARVIN-500 insecticide on cotton and soybeans. LARVIN-500 is also known by the acronym UC51762. Its chemical formula is:

Dimethyl N,N'-[thiobis[(methylimino)carbonyl oxy]]bis [ethanimidothioate]

and its chemical structure is:

$[(CH_3)\ C{=}N{-}OCO{-}N(CH_3)\ ]_2S$

SCH_3

UC51762 contains 44% of the above chemical as active ingredient and 56% inactive ingredients. Each quart contains 500 g/l or 1.045 lb a.i /qt. (4.18 lb A/gal). The reported physical and chemical properties of UC51762 are:

1) Form: crystalline powder

2) Color: white

3) Odor: Slightly sulfurous

4) Melting point: 173-174°C

5) Vapor pressure: 4.3×10^{-5} mmHg at 20°C, 4.2×10^{-4} mmHg at 50°C

6) Solubility in water: approximately 35ppm at 25°C

7) Stability: very stable in light and ambient conditions

8) Rate of hydrolysis at 10ppm concentration and 25°C: pH 3 = half-line 8.62 day, pH 9 = 0.89 day, pH 6 = approx. 3% loss in 9 days.

9) Octanol/water partition coefficient: Log P by reverse-phase TLC=1.65

1.2 Experimental Plan (Section G)

The applicant is proposing to test LARVIN in 20 of the major producing cotton and soybeans states - 33 locations for cotton and 28 for soybeans.

Total numbers of acres involved in the experiment is 280 for soybeans and 730 for cotton. The cotton acreage includes a location in Arkansas of 400-acre pest management program.

2. Directions For Use

The proposed label (Section B) provides the following:

2.1 Rate of Application:

On Cotton: Use 11 to 29 fl. oz/acre for early infestations and newly hatched larvae. As worm pressure increases, dosage should be increased from 15-22 oz/acre.
PHI: Do not apply less than 7 days before harvest.

On Soybean: Use 7.5 to 15 fl. oz/acre; and apply when insects or worm populations begin to cause economic damage. Repeat application at this rate of increase, depending on infestation.
PHI: Do not apply less than 28 days before harvest.

2.2 Method of Application

Apply when insects just appear. Repeat as needed, usually at 5 to 7 day intervals for most pests.

2.3 Disposal

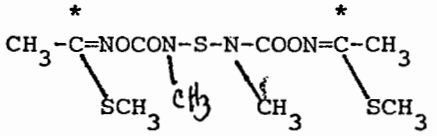
Rinse empty container thoroughly with water. Crush and bury in authorized site for pesticide containers. NEVER REUSE CONTAINER. STORE UNUSED PRODUCT IN DRY, LOCKED AREA.

2.4 Precautionary Statement

Keep away from ponds, lakes or streams. Do not contaminate bodies of water when cleaning spray equipment or disposing of waste. Do not apply where runoff is likely.

3. Discussion of Data

The radio labeled UC51762 used in the following studies is labeled as follows: (* denotes ^{14}C position).



3.1 Hydrolysis of UC51762 in Aqueous Buffer Solutions-(EPA Registration No. 0976647) by N.R. Andrames and R. H. Bailey

The rates of hydrolysis of 10ppm of UC51762, acetadelehyde-1-^{14}C and the nature of the hydrolytic products were studied in aqueous buffer solutions adjusted to 3 different pH

levels (basic, neutral, acridic). The study was conducted in the dark for a period of 9 days at 25°C. Samples from six incubation intervals were examined by TLC and radiochemical analysis, and the results reported as follows:

Hydrolysis in pH3 Aqueous Buffer Solution at 25°C

Products	% of the recovered radioactivity			
	0 hr	1 day	4 days	9 days
UC51762	98.2	92.7	77.0	47.6
Methomyl	1.8	7.3	22.4	50.9
Methomyl Oxime	ND 1/	ND	0.5	0.6
Unknowns	ND	ND	ND	0.6
Origin of TLC 2/	T 1/	T	0.1	0.2
Water solubles	T	T	0.1	0.1
ppm ^{14}C-UC51762 Equivalents	10.00	10.02	9.92	9.63

1/ ND=none detected
T = Detected amounts of less than 0.1%

2/ Radioactivity remaining at the point of applicaton of the organic extracts to the TLC plates.

Hydrolysis in pH6 Aqueous Buffer Solution at 25°C

Products	% of the recovered radioactivity			
	0 hr	1 day	4 days	9 days
UC51762	99.0	98.6	97.2	96.0
Methomyl	0.9	1.4	2.5	2.9
Methomyl Oxime	ND	ND	0.3	0.7
Unknowns	ND	ND	ND	0.3
Origin of TLC	0.1	0.1	T	0.1
Water solubles	T	T	T	T
ppm ^{14}C-UC51762 Equivalents	10.00	10.02	9.78	9.91

Hydrolysis in pH9 Aqueous Buffer Solution at 25°C

Products	% of the recovered radioactivity			
	0 hr	1 days	4 days	9 days
UC51762	97.9	44.5	4.4	0.3
Methomyl	1.8	44.4	79.3	61.8
Methomyl Oxime	0.3	3.6	3.8	21.1
Unknowns	ND	ND	0.8	0.7
Origin of TLC	0.1	5.7	9.7	14.4
Water solubles	T	1.8	2.0	1.7
ppm ^{14}C-UC51762 Equivalents	10.00	9.99	10.03	10.03

Conclusion

The above results indicate that UC51762 is stable at pH6 (only 3% degradation in 9 days), while hydrolyzes rapidly at pH=9 (t1/2=0.89 d) and moderately at pH=3 (t1/2=8.62 d), both through cleavages of N-S-N skeleton.

Methomyl is the major hydrolytic product at all pH levels. Though it is relatively stable in pH3 and 6, methomyl hydrolyzes further to form methomyl oxime in pH9.

3.2 Photochemical Transformation of UC51762 by N.R. Andrames and P.R. College (EPA Reference #097647)

In temperature range of 20-25°C, and pH6, the photolysis of UC51762 acetaldehyde -1-^{14}C solution containing 5ppm of the compound was examined under ultraviolet light (>290nm). The reaction was observed in the presence and absence of 2% acetone as a triplet sensitizer as well as in the dark for a testing period of 12 days. Radiochemical and TLC analysis of samples examined at various intervals showed the following results:

Dark Reaction of UC-51762-acetaldehyder 1-^{14}C

Products	% of the recovered radioactivity			
	0 hr	3 days	9 days	12 days
UC51762	98.7	97.6	95.0	94.9
Monosulfoxide	0.2	0.2	0.2	0.2
Methomyl	1.0	2.0	4.3	4.2
Methomyl Oxime	ND	ND	0.3	0.3
Unknowns	ND	ND	0.4	ND
Origin of TLC	0.1	0.1	0.2	0.4
Water solubles	T	0.1	0.1	0.1
ppm ^{14}C-UC51762 Equivalents	5.0	5.1	5.1	5.1

Photolysis of ^{14}C-UC51762 in pH6 Buffer Solutions

Products	% of the recovered radioactivity			
	0 hr	3 days	9 days	12 days
UC51762	98.3	94.0	90.1	88.7
Monosulfoxide	ND	1.3	2.0	2.5
Methomyl	1.5	4.0	5.7	7.1
Methomyl Sulfoxide	ND	ND	0.2	0.3
Methomyl Oxime	ND	ND	0.3	0.3
Methomyl sulfoxide oxime	ND	ND	ND	0.4
Unknowns	0.2	0.4	1.2	0.3
Origin of TLC	T	0.2	0.3	0.2
Water solubles	T	0.2	0.3	0.4
ppm ^{14}C-UC51762 Equivalents	5.0	5.0	5.0	5.0

Photolysis of ^{14}C-UC51762 in pH6 Buffer Solutions in the presence of acetone

Products	% of the recovered radioactivity			
	0 hr	3 days	9 days	12 days
UC51762	97.3	81.4	66.6	62.3
Monosulfoxide	ND	5.0	7.2	5.2
Methomyl	1.9	8.4	14.5	15.9
Methomyl Sulfoxide	ND	0.6	1.4	1.5
Methomyl Oxime	ND	0.3	0.3	0.6
Methomyl sulfoxide oxime	ND	0.5	0.8	0.9
Unknowns	0.8	2.6	3.2	2.3
Origin of TLC	0.1	0.5	0.7	0.7
Water solubles	T	0.7	1.2	1.8
ppm ^{14}C-UC51762 Equivalents	5.0	5.0	4.8	4.6

Conclusion

The above results show UC51762 is stable in the dark (4% degradation in 12 days), while it degrades extensively in the light and at higher rate in the presence of triplet sensitizer (acetone). The measured t1/2 is 80.91 d and 18.65 d in absence and presence of the sensitizer, respectively.

Methomyl appears to be the major photolysis product accompanied by moderate amounts of UC51762 monosulfoxide and minor amounts of methomyl oxime, methomyl sulfoxide, and methomyl sulfoxide oxime.

3.3 UC51762 Photodegradation on Soil Surfaces by A.M. Khasawinah and P.R. College (EPA Reference #097647)

The photodegradation of UC51762 - ^{14}C on soil was investigated on three different soil types under lab conditions. Soils composition is as follows:

Soil location → / Parameters ↓	Silt clay loam Salinas, Clif.	Norfolk sandy loam Clayton, N. Carolina	Sandy loam Edcouch, TX
PH	8.1	5.8	7.8
% Org. matter	1.3	0.8	1.0
% Sand	25	83	65
% Silt	42	15	17
% Clay	33	2	18
Field Moisture Cap	33.0	17.6	24.7
Ca ppm	3200	350	2100
Mg "	750	73	240
Na "	130	48	190
K "	180	56	450

Soil samples were treated, for both dark and light reactions, at a rate of 1.0 lb/A (11.4 $\mu g/cm^2$) at 25°C, irradiated with ultraviolet (nm>,290), incubated and sampled at various time intervals. The reported results of the radioactivity and TLC analysis are as follows:

Photolysis of ^{14}C-UC51762 on Norfolk Soil

	Period of Photolysis (hr)	% Distribution of C-14 Extracted	Unextracted	Volatile	% of extractable *C-14 by TLC H_2O/Origin	MSM	M	MO	M_1
ght Retn:	0	100	-	-	<1	87	6	<1	ND
	8	38	1	61	2	29	4	<1	ND
	16	21	1	78	<1	15	3	ND	<1
	24	16	1	83	<1	12	2	ND	<1
rk Retn:	0	100	-	-	-	87	6	<1	ND
	12	99	1	-	<1	86	8	<1	<1
	24	89	1	10	<1	77	7	<1	<1

)ther extractables were identified but not verified.
:M = UC51762

= Methomyl $CH_3NHCOON=C(SCH_3)-CH_3$
) = Methomyl Oxime $CH_3 - C(SCH_3) = N - OH$
= Methomyl Sulfoxide $CH_3 - C(=O)(SCH_3) = N - OH$

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Photolysis of ^{14}C-UC51762 on California Soil

	Period of Photolysis (days)	% Distribution of C-14 Extracted	Unextracted	Volatile	% of extractable *C-14 by TLC H_2O/Origin	MSM	M	MO
ght Rctn:	0	100	-	-	<1	~~80~~	~~9~~	~~4~~
	1	95	1	4	<1	60	14	7
	14	82	1	17	<1	73	7	<1
	28	85	2	13	<1	69	11	2
rk Rctn:	0	100	-	-	~~ND~~	80	10	3
	7	100	-	-	ND	80	11	2
	28	100	-	-	<1	81	9	3

Photolysis of ^{14}C-UC51762 on Texas Soil

	Period of Photolysis (days)	% Distribution of C-14 Extracted	Unextracted	Volatile	% of extractable *C-14 by TLC H_2O/Origin	MSM	M	MO
ght Rctn:	0	100	-	-	ND	~~81~~	~~7~~	~~4~~
	1	98	2	-	1	26	37	16
	14	79	3	18	3	45	26	1
	28	70	2	28	6	20	30	2
rk Rctn:	0	100	-	-	ND	81	7	4
	7	100	-	-	ND	74	12	5
	28	100	-	-	ND	74	13	3

No ^{14}C loss during treatment periods was noted.

Conclusion

Evident from the above results that light accelerates UC51762 degradaton on soils surface into methomyl, methomyl oxime, and methomyl sulfoxide with eventual break down to volatile product (acetonitrile is the concluded probability). The degradation is much greater in a light textured soil (such as Norfolk) than in heavier textured soils (such as Calif. and Texas soils) where the pesticide is strongly adsorbed, more protected from light action and thus more stable. It was observed that the soil pH did not contribute to the pesticide degradation on soil surface. (On Norfolk soil at pH5.8, UC51762 rapidly degraded, while it was found stable in solution at same pH.)

3.4 Mobility - Rapid Leaching

Mobility on Soil Thin Layer Chromatograms by A.M. Khasaminah and G.C. Holsing (EPA Reference #097647)

The mobility of ^{14}C - UC51762, and its major soil degradation products methomyl and methomyl oxime, on soil TLC was compared to other agrichemicals of known mobility on soil TLC plates. Testing was done on four different soil types (Norfolk, California, Texas and Muskingum). The characteristics of Norfolk, Calif., and Texas soils are known, the Muskingum silt loam (from Ohio.) soil contents are:

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PH	% org. matter	% sand	% silt	% clay	field moisture cap
5.4	1.3	38	42	20	20.5

The calculated mobility of U51762 and its soil degradation products, and reference pesticides on four different soil of TLC plates are as follows:

Compund	Norfolk Sandy loam R_f	California Silt Clay loam R_f	Texas Sandy loam R_f	Muskingum Silt loam R_f
UC51762	0.21 ± 0.01	0.12 ± 0.01	0.12 ± 0.02	0.08 ± 0.00
Methomyl Oxime	0.89 ± 0.01	0.86 ± 0.09	0.93 ± 0.02	0.88 ± 0.04
Methomyl	0.77 ± 0.01	0.64 ± 0.04	0.79 ± 0.02	0.73 ± 0.03
Diquat	0.00	0.00	0.00	0.00
2,4-D	0.52 ± 0.01	0.68 ± 0.03	0.82 ± 0.03	0.60 ± 0.05
2,4,5-T	0.39 ± 0.01	0.60 ± 0.00	0.73 ± 0.03	0.41 ± 0.04

R_f = front of streak (Spot) / water front

Conclusion UC-51762 exhibited very low mobility with small leaching depth on the four soils with R_f values ranging from 0.08-0.21, and ranking between class 1 and class 2 (immobile-low mobility) on Helling and Turner (1968) classification scale for pesticides mobility on soil TLC plates. Highest mobility of UC51762 was observed on soils with higher sand contents.

Methomyl mobility was rated class 4 on all soils tested (i.e. higher mobility than UC51762), and methomyl oxime had the highest mobility.

3.5 Metabolism

Soil Aerobic, Anaerobic, Sterile

Fate of UC51762 in Soils by A.M. Khersawinah

The fate of ^{14}C-UC51762 in the three soil types (Norfolk, California, and Texas), from 0 - 10 cm profile, was investigated under aerobic, anaerobic and sterile conditions. The pesticide applied at 1 ppm concentration and incubated up to 28 days at two temperatures.

The reported results of radio-assay, extraction, separation and TLC identification of metabolites are as follows:

Decomposition of ^{14}C-UC51762 (1 ppm) in Texas Soil Under Aerobic Lab. Condition

Incubation (Period (days))	^{14}C% Distribution			% TLC Analysis of ^{14}C extract						
(Field Fresh Soil) at 25 ± 1°C	Extract*	Unextract	Volatile**	Origin	MSM	M	M_1	MO	M.O	M_2
0	95			<1%	76	21	<1%	2	-	-
7	32	26	42	3	3	4	"	77	3	<1%
9	15	31	54	3	7	8	"	54	2	"
14	4	26	70	6	16	15	"	49	4	"
20	2	19	79							
57	1	18	81							
(Sterile Soil) 25 ± 1°C										
8	100		0		11	87		3		
27	98	8	0		2	85		12		
36	88	14	0		3	82		12		
57	97	10	0		3	78		18		
62	85	22	0		14	79		6		
(Semiaerated Soil) 25 ± 1°C										
1	98	4	0		52	47		1		
12	79	14	8		3	57	<1%	36	1%	
29	40	22	38		7	57		36	"	
36	12	23	64		11	48		37	"	
57	4	22	74		64	26	<1%	4	"	
(Activated Soil) 25 ± 1°C										
2	31	15	54	2	11	70	<1%	7		
5	5	33	62	7	37	48		8		
9	12	29	49	<1%	87	"	"	1%		
14	3	27	70							
(Activated Soil) 15°C										
2	69	9	22	<1%	15	81	<1%	3		
6	66	21	11		2	81	"	15	<1%	
9	4	31	65							
14	3	22	75							

Decomposition of ^{14}C-UC51762 (1 ppm) in Norfolk Soil Under Aerobic Condition

Incubation Period (days)	^{14}C % Distribution			% ^{14}C Extractables TLC Analysis						
(Field Fresh Soil) 25 ± 1°C	Extract*	Unextract	Volatile**	Origin	MSM	M	M_1	M_2	MO	M.O
0	90			<1%	67	28			2	
12	5	15	80	4	63	26	<1%		6	
28	3	18	79	2	66	29			4	
35	2	8	90	1	57	33	<1%		6	
(Greenhouse activated) 25 ± 1°C										
1	87	7	6	<1%	12	84	<1%		2	
3	45	14	41	"	16	75	"		3	
8	29	19	52	"	7	89	"	<1%	2	<1%
20	7	20	73	9	20	60	2		2	
(Greenhouse activated) 15°C										
1	99	3	0	<1%	26	73			<1%	
6	75	8	17	"	9	89	<1%		"	<1%
8	78	11	11	"	11	87			2	
20	20	55	17	28	10	88	"		<1%	

* Almost all organsoluble (water fraction 1%)

** Presumably CO_2, determined by difference

Decomposition of ^{14}C-UC51762 (1 ppm) in California Soil Under Aerobic Condition

Incubation (Period (Days))	Extract*	Unextract	Volatile**	Origin	MSM	M	M_1	MO	M.O	M_2
(Fresh Field) 25 ± 1°C										
0	100				83	13	<1%	<1%	1	<1%
7	32	24	44	<1%	9	86	"	"	1	
29	14	25	61	"	5	89	2	"	2	<1%
36	8	24	69	"	6	86	2	"	2	"
(Greenhouse Activated) 25±1°C	9	27	64	"	10	86	2	"	1	"
3	82	15	3	<1%	10	86	<1%	<1%	2	<1%
10	32	27	31	<1%	10	85	"	2	2	"
13	36	29	35	"	7	89	"	<1%	<1%	"
16	13	33	54	2	14	82	"	"	"	"
(Greenhouse activated) 15°C										
3	100	6	0	<1%	22	76	<1%		2	
10	54	23	23	"	9	87	"	<1%	2	<1%
13	48	25	27	"	10	86	"	"	1	"
16	48	24	28	"	6	92	"	"	1	"

* defined previously
**defined previously

$^{14}CO_2$ Evaluation from ^{14}C-UC51762 Treated Soil (Texas Soil)

Time (days)	0	7	24	28	43	90
CO_2%	0	29	67	73	69	72

At end of incubation 2% was extractable and 27% was unextractable, total recovery 96%.

Decomposition of ^{14}C-UC51762 in Soils Under Lab. Anaerabic Conditions 25 ± 1°C

Incubation Period (day)	% Distribution of ^{14}C				
	Extract				
Texas field fresh soil (1 ppm)	Organ Soluble*	Water Soluble	^{14}C-CH_3CN	Unextracted	Volatile**
7	78	1	2	9	10
20	5	6	35	15	40
28	3	12	24	15	47
40	8	1	10	10	72
Texas Greenhouse Activated (10 ppm)					
9	4	1	62	13	20
14	2	4	55	7	33
California Greenhouse Activated (10 ppm)					
9	5	6	59	22	16
14	2	2	43	20	34

* Mostly polar material
**Presumably CH_3CN

Organic Matter Fractionation of Soil

Unextracted Radioactivity

Treatment	Unextracted ^{14}C % of Original	% Distribution of Unextracted Fulvic	Humic	Humin
Texas Soil				
Fresh, 25°C				
30 days	20	65	4	30
58 days	18	55	3	38
Activated, 25°C				
9 days	29	58	5	31
15°C, 15 days	31	63	5	16
Fresh, anaerobic, 25°C, 40 days	10	66	7	30
Sterile, 25°C,				
17 days	11	99	1	0
62 days	22	97	1	1
California Soil				
Fresh, 25°C,				
20 days	25	52	2	46
44 days	27	63	2	36
Activated, 25°C,				
16 days	24	62	2	30
15°C, 16 days	33	60	4	32
Norfolk Soil				
Fresh, 35 days	8	81	5	17
Activated, 25°C,				
20 days	17	77	4	22
15°C, 20 days	20	92	1	10

Conclusion

Concluded from the above results that:

1) The degradation of UC51762 in soils is the result of biological and non-biological factors and proceeds via biological breakdown to methomyl which hydrolyzes to the oxime (unstable) and then completely breaks down to volatiles. It occurs rapidly at 25°C (1/2<week), but slower at lower temperature (15°C), yielding practically same metabolic products in the 3 soil types. It was noted that the slower degradation was prominent during the first 10 days of incubation and accelerated afterwards suggesting a lag phase for the microbial build up. This lag phase was shorter in the Texas soil.

2) In sterile and non-sterile soil, UC51776 degraded rapidly by cleavage of N-S-N skeleton to methomyl which then hydrolyzed more slowly to its oxime. Methomyl accounted for approximately 80% of the total soil residue.

3) Volatiles accounted for the major products of UC51762 degradation in soils under aerobic and anaerobic conditions. Under aerobic conditions it was extensively degraded to CO_2; CO_2 was the only volatile product. Under anaerobic conditions, CH_3CN was the volatile product encountered, excluding CO_2, while the non-volatile residue consisted of polar materials.

4) The total organosolubles were found to decrease to levels of <1% of the initial application. Under aerobic conditions organosoluble residue was found to consist mainly of UC51762, methomyl and methomyl oxime with methomyl constituting the main product in the soil extracts. While methomyl oxime was found in insignificant amounts, other products: methomyl oxime sulfoxide, methomyl sulfone, methomyl sulfoxide, and methomyl oxide sulfone were found in minor amounts.

5) Up to 50% of radioactive losses encountered during chromatography had been attributed to the probable presence of CH_3CN residue which is known from the literature to metabolize by microorganism into natural products of Kerb's cycle that are water soluble. The relative percentage of the water solubles was found to increase although the overall extractables declined with time.

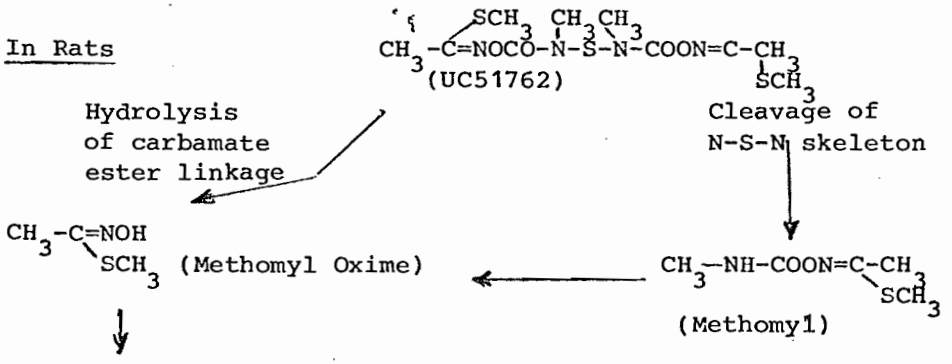
6) The unextracted metabolites increased gradually with incubation time then declined slowly after reaching a plateau at about 30% of the initial application. Some of the unextractables were found as bound residues of methomyl and its oxime.

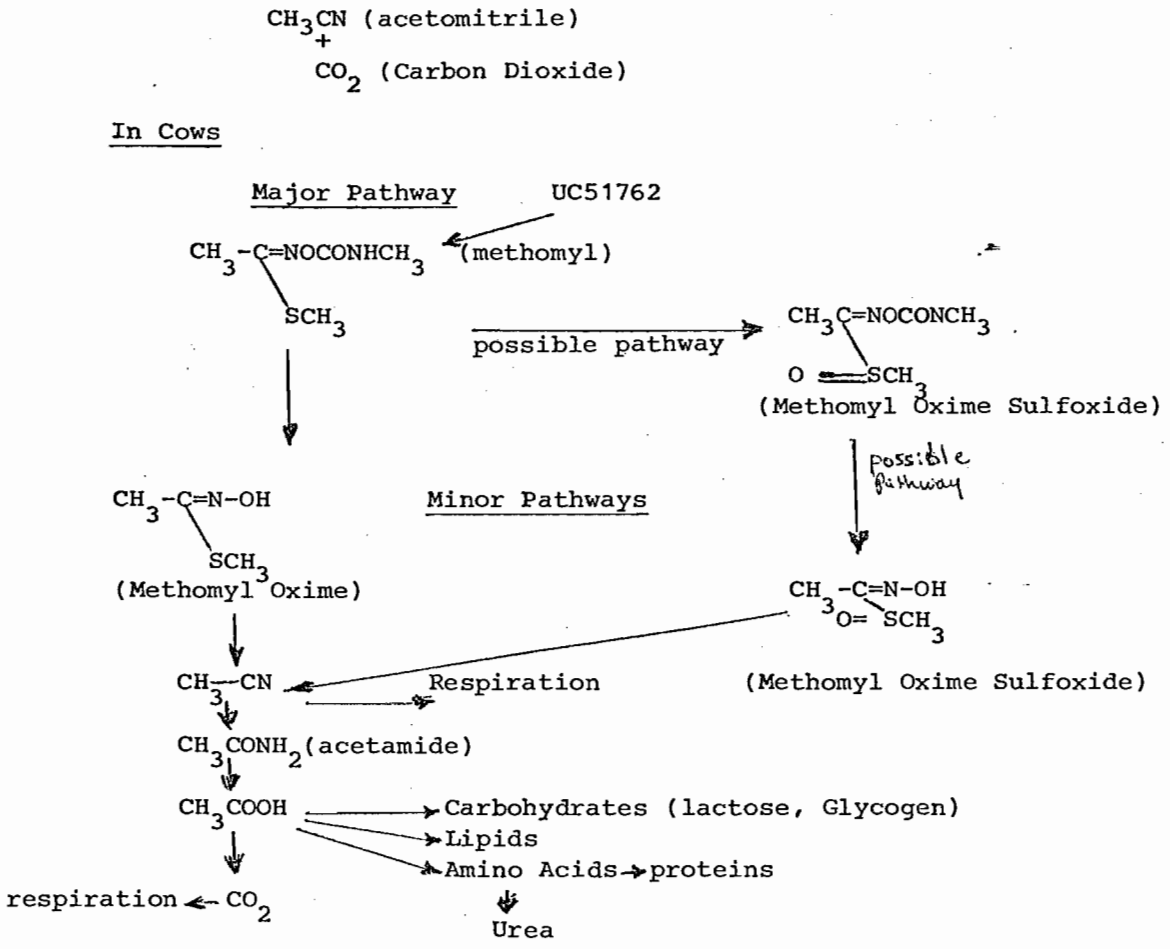
It was determined that the unextracted metabolites represents mostly ^{14}C fixed by soil microflora.

3.6.2 Metabolism in Animals (not required by EFB but gives useful information)

The metabolism of ^{14}C-UC51762 in animals (rats and a lactating cow). The registrant proposed the following metabolic pathways.

In Rats




CH3CN (acetomitrile)
+
CO2 (Carbon Dioxide)
In Cows
Major Pathway
UC51762
CH3-C=NOCONHCH3
(methomyl)
SCH3
possible pathway
CH3C=NOCONCH3
O
SCH3
(Methomyl Oxime Sulfoxide)
possible pathway
CH3-C=N-OH
SCH3
(Methomyl Oxime)
Minor Pathways
CH3-C=N-OH
O=
SCH3
(Methomyl Oxime Sulfoxide)
CH3-CN
Respiration
CH3CONH2(acetamide)
CH3COOH
Carbohydrates (lactose, Glycogen)
Lipids
Amino Acids→proteins
Urea
respiration ← CO2

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In the rat's study, 34% of the measured radioactivity could not be accounted for at 15 minutes after treatment and was assumed to be lost as volatiles, while the remaining 66% were distributed as follows:

Body Fraction	% of Applied Dose
Alimentary Canal (Tissues + Contents)	40.3
Kidney	1.2
Lung	0.3
Liver	3.3
Spleen	0.1
Muscle	0.8
Heart	0.1
Fat	0.1
Plasma	1.0
Red Blood Cells	2.8
Remaining Carcass	16.0
Total Recovered	66.0

Radioactivity in the stomach contents identified indicated the presence of organsolubles consisting of UC51762 (59.42%), methomyl (31.37%) and methomyl oxime (2.22%) and three unknown organsolubles metabolites accounting for 1.4%. The balance (4.39 %) was identified as water solubles.

In the Cow's study, the accumulative percent of the dose after 3 days is:

^{14}C-label in:	Feces	Urine	Milk	Tissues	Respiratory Gas
%	11.4	5.0	4.6	10.1	66.2

The radioactivity retained in the tissues was mostly concentrated in the liver.

No UC51762 or its initial metabolite (methomyl) were detected in milk or tissues; however, they were found only in small amounts in the feces. Residues found in milk were acetonitrile, acetamide and natural products. In tissues, radioactivity was found to be mostly ^{14}C- proteins in addition to ^{14}C- gylcogen, acetonitrile and acetamide. Urea was isolated from urine.

3.63 Metabolism in Plants (not requested by EFB, but gives useful info.)

The metabolism of UC51762 in cotton, soybeans, corn, wheat cabbage and carrot plants was studied. Based on the findings of various studies, the following metabolic pathway of UC51762 in plants has been proposed by the registrant.

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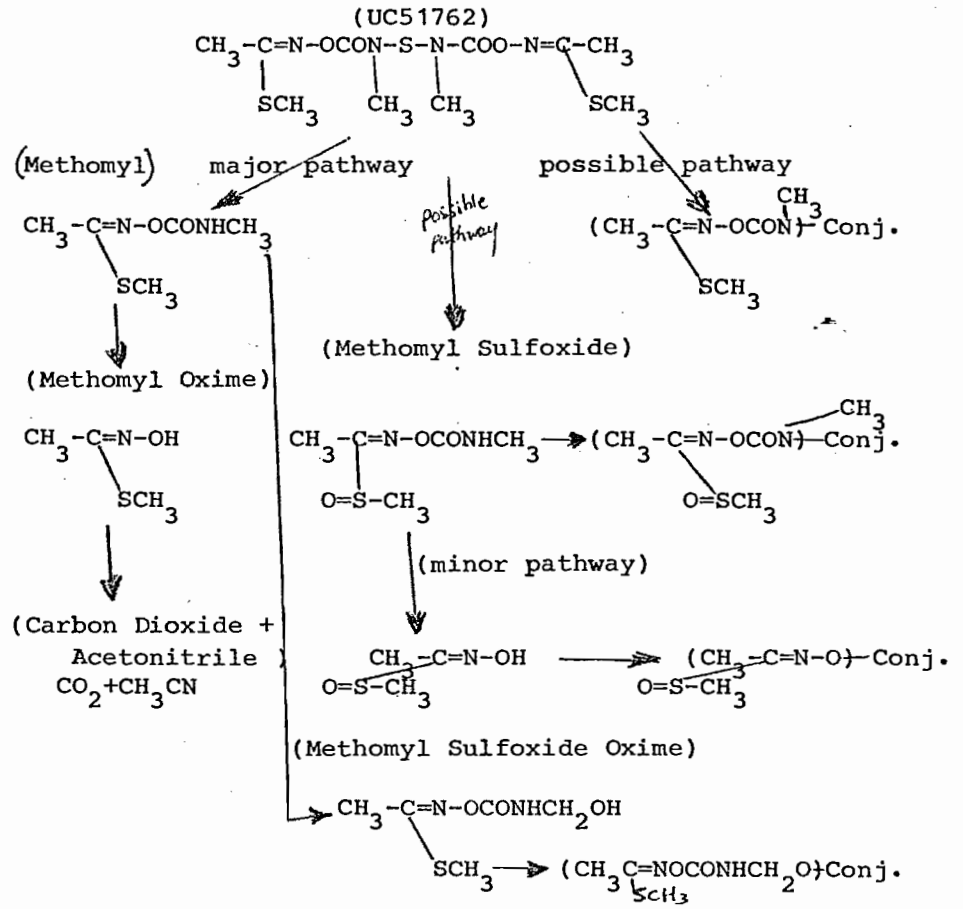


The metabolism of UC51762 in several species of plants and in plant callus tissue has been shown to follow a consistent pattern. Three metabolic pathways have been identified. First, UC51762 is rapidly metabolized by plants forming methomyl as the initial metabolic product. Methomyl subsequently hydrolyzes to methomyl oxime which is believed to convert quickly to carbon monoxide and aceto-nitrile, the end products of UC51762 main metabolic pathway. The other metabolic pathway is the minor one and involves oxidation of methomyl to methomyl sulfoxide and hydroxlation to the methylol of methomyl.

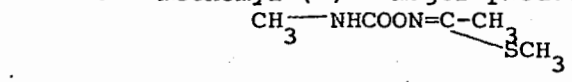
All of the intermediate metabolites of UC51762, namely methomyl, methomyl oxime, methomyl sulfoxide and methomyl methylol are further metabolized by conjugation, (possible third metabolic pathway) to form water soluble products.

4. Conclusion

4.1 UC51762 hydroxlysis in solutions at 25°: pH of 9 (t1/2 = 0.89 d), pH of 3 (t1/2 = 8.62 d), and pH of 6 (3% loss in 9 days).

The hydrolytic products identifiable at the three pH levels are:

a. methomyl (M) - major product, t1/2 = 9.99 d



b. methomyl oxime

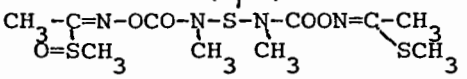
, and

c. Water soluble product, of ≤2%

4.2 UC51762 photodegrades in solutions containing 5 ppm at pH 6 and in temp. range 20-25°, much faster in presence of a triplet sensitizer (acetone) with t1/2 = 18.65 days, while t1/2 = 80.91 days in absence of the sensitizer.

The photolysis products identifiable under both conditions are:

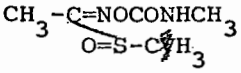
a) monosulfoxide (MSM)-minor



,

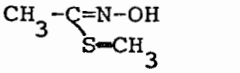
b) methomyl(M)-major ,

c) methomyl sulfoxide (M)-minor



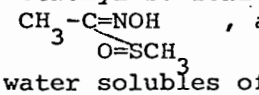
,

d) methomyl oxime (MO)-minor



,

e) methomyl sulfoxide oxime (MO)-minor



, and

f) water solubles of ≤4%

Degradation of the insecticide under the above conditions in darkness was found to be minimal (≈4% degradation in 9 days.)

4.3 Photogradation on soil surfaces

Light was found to accelerate UC51762 degradation in light textured soil (i.e. Norfolk soil sand contents 86% and clay contents 2%) at much faster rate (t1/2=8 hr.) than in heavier textured soils (i.e. Calif. & Tex. soils). It was also found to adsorb strongly to the clay and becomes more protected from the light action and thus more stable.

When applied to soils at rate of 1.00 lb/A at 25°C temp, UC51762 photodegrades in light, yielding extractable products (majority), unextractable (≤3%) with eventual break down to volatiles probably acetonitrile CH_3CN. Extractable products consisted mainly of:

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a) UC51762 (MSM)-major

b) methomyl (M)

c) methomyl oxime (MO), and

d) methomyl sulfoxide (M) <1%

4.4 Leaching of UC51762 measures between class 1 and 2 (immobile low mobility) on Helling and Turner (1968) classification scale. Methomyl mobility is class 4 while methomyl oxime measures the highest mobility, class 5. Variation in the mobility of these products on the soil types was generally small.

4.5 In the three different soil types, methomyl is the primary product of UC51762 degradation irrespective of the treatment variables (sterile vs. nonsterile, aerobic vs. anaerobic, 15 vs. 25 ^{o}C temp.). The half life of this conversion is less than two days. Methomyl is extensively degraded in non-sterile soils forming either CO_2 or CH_3CN under aerobic and anaerobic conditions, respectively. These volatile end products accounted for at least 70% of the initial treatment after 14 days of incubation in most cases, while extractable residues declined rapidly to less than 2% in 14-28 days. These residues consisted mostly of UC51762, methomyl and its oxime in aerobic soils and polar materials in anaerobic soils. Unextractable residues (fulvic, humin, and humic), on the other hand, increased gradually and plateaued at 20-30% of the initial treatment and found incorporated into the soil organic matter.

4.6 Use of methomyl, as labeled by other pesticide manufacturers, does not warrant any rotational crop replant restrictions.

4.7 Presence of UC51762 major and minor degradates in the environment:

a) Methomyl (major) (UC45650) S-methyl-[methyl carbamoyl)oxy]thio-acetimidate $CH_3-C(=NOCONHCH_3)-SCH_3$ found in plant's leaves, animal body tissues and fluids, top 0-10 cm in soil profile, aqueous solution at pH 3&9 and at pH 6 in photolyzed soil.

b) Methomyl oxime (UC52702) S-methyl-N-hydroxy thio-acetimidate $CH_3-C(=N-OH)-SCH_3$ accompanies methomyl in minor amounts, as above.

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c) methomyl sulfoxide 1-methyl sulfonyyl-N-[(methyl carbamoyl) oxy] acetimidate
$CH_3-C(=N-OCONHCH_3)-O=SCH_3$
accompanies methomyl and its oxime in very small amounts in animals, plants, and soils.

d) CH_3CN acetonitrile and CO_2 Carbon dioxide — End products detected in soils, plants, and animals metabolic pathways.

e) Monosulfoxide (UC51762) — Found in pH 6 buffer solution exposed to light (nm>290).
$CH_3-C(=NOCON(CH_3)-S-N(CH_3)-COON=C(-CH_3)-SCH_3)-O=SCH_3$

f) methomyl sulfoxide oxime (UC54169) — S-methylsulfimyl-N-hydroxyacetimidate
$CH_3-C(=N-OH)-O=SCH_3$, found in very small amounts in plants and animals.

4.8 The reported physical and chemical properties of UC51762 are:

1. Form = crystalline powder
2. Color = white
3. Odor = Slightly Sulfurous
4. Melting Point = 173-174°C
5. Vapor Pressure = 4.3×10^{-5} mostly at 20°C, 4.2×10^{-4} mostly at 50°C
6. Solubility in water : 35 ppm at 25°C
7. Octanol/water partition coefficient = Log P by reverse-phase TLC=1.65

5. Recommendation

5.1 The fate of UC51762, as reported, and its major degradate methomyl, is known to support the use under this permit.

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5.2 Note to EEB: It should be noted that the metabolic pathways investigated for this permit established the formation of methomyl as the primary product of UC51762 degradation through rapid hydrolytic cleavage of N-S-N skeleton; it is presumed;therefore, that each UC51762 molecule would yield 2 molecules of methomyl.

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Madeline Nawar M. Nawar 3/1/79
Review Section 1

Table 2. Summary of Environmental Chemistry Data Requirements by Intended Use Pattern.

Data Requirements*	Terrestrial Uses										Aquatic Uses				Terrestrial/ Aquatic Uses	Aquatic Impact Uses					
	Domestic Outdoor		Green-House		Non-Crop		Tree Fruit-Nut Crop		Field-Veg. Crop		Aquatic Food Crop		Aquatic Non-Crop		Forest	Direct Discharge		Indirect Discharge		Wastewater Treatment	
Physico-Chemical Degradation																					
Hydrolysis	X	-	X	-	X	-	X	-	X	-	X	-	X	-	X	-	X	-	X	-	X
Photodegradation		-		-	X	-	X	-	X	-	X	-	X	-	X	-	X				
Metabolism																					
Aerobic Soil	X	-	X	-	X	-	X	-	X	-		-		-	X						
Anaerobic Soil		-		-		-		-	X												
Anaerobic Aquatic		-		-		-		-		-	X	-	X	-	X	-	X				
Aerobic Aquatic		-		-		-		-		-	X	-	X	-		-	X				
Effects of Microbes on Pesticides		-		-	X	-	X	-	X	-	X	-	X	-	X	-	X				
Effects of Pesticides on Microbes		-		-	X	-	X	-	X	-	X	-	X	-	X	-	X				
Activated Sludge		-		-		-		-		-		-		-		-		-	X	-	X
Mobility																					
Leaching		-		-	X	-	X	-	X	-		-		-	X						
Adsorption	X	-	X	-	X	-	X	-	X	-	X	-	X	-	X	-	X				
Volatility		-	X	-		-		-		-		-		-	X						
Field Dissipation																					
Soil	X	-		-	X	-	X	-	X	-	X	-		-	X						
Water		-		-		-		-		-	X	-	X	-	X	-	X				
Forest		-		-		-		-		-		-		-	X						
Accumulation																					
Rotational Crop		-		-		-		-	X	-	X										
Irrigated Crop		-		-		-		-		-	X	-	X								
Fish		-		-	X	-	X	-	X	-	X	-	X	-	X	-	X				
Special Study		-		-		-		-		-		-	X								

*Data requirements cited in §163.62-10(c)(3), (f) and (g); §163.62-11(e); §163.62-12; and §163.62-13 are not included in this table.