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To: Coordination Branch

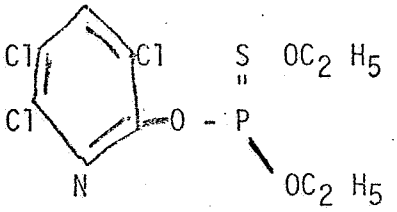
Subject: Evaluation of Environmental Data for Chlorpyrifos [O,O-diethyl O-(3,5,6-trichloro-2-pyridyl) Phosphorothioate] (Dursban) - PP. No. 3F1306, Reg. No. 464-ULN, UUA, UUI, UUO, UUT - Dow Chemical Company - Filed October 10, 1972

INTRODUCTION

1. This is the first environmental review for the insecticide chlorpyrifos. Other names trichloropyrphos, lorsban, Dowco 179, Ent. 27311.

2. Chemistry of chlorpyrifos

Structure



Emp. Form: $C_9 H_{11} Cl_3 NO_3 PS$

Mol. Wt: 350.6

Form: Granular crystalline solid

Color: White

Odor: Mild mercaptan

Melting Pt: 41.5 - 43.5°C

Vap. Pres: 1.87×10^{-5} mm Hg at 25°C
8.87×10^{-5} mm Hg at 35°C

Solubilities:

Solvent	g chlorpyrifos/100g at 25°C
Acetone	650
Benzene	790
Carbon tetrachloride	310
Chloroform	630
Diethyl ether	510
Isooctane	79
Methanol	95
Xylene	Ca 400
Water	0.0002

Stability: Stable under normal storage. Stable for several weeks in neutral or acidic aqueous formulation at or slightly above room temperature. Chemical breakdown increases as temperature and pH increases.

Partition coefficient, n-octanol/water 66,600.

Hydrolysis: 50% v/v methanol/water at 23°C.

pH	1/2 Life Days
5	1,100
6	1,600
7	350
8	55
9	30

DISCUSSION OF DATA (SEC. D-29)

1. Persistence and Degradation. Ref. 38 - 2,6-^{14}C study.

PPM Added	Initial PPM Extracted	30 Weeks PPM Extracted	30 Weeks PPM Bound	Soil
4.24	3.9 (91.9%)	1.1 (25.9%)	1.4 (33%)	Sandy Loam
4.24	4.0 (94.3%)	3.0 (70.7)	.6 (14.1%)	Sandy Loam (sterile)
4.24	4.4 (103.7%)	1.4 (33.0%)	.9 (21.2%)	Clay Loam
2.12	2.6 (122.6%)	.7 (33.0%)	.7 (33.0%)	Sandy Loam
5.0		.7 (14.0%)	.5 10.0%	Clay
5.0	5.3	3.7 (74.0)	.2 (4.0%)	Silt

Soil in jars at 65-95°F, moisture 15-20%. Sandy loam planted to sugarcane.

Conclusions

A. In 5 soils at 30 weeks the 1/2 life had not been reached.
B. The loss in clay soil is not understood.
Data in ppm should be submitted at each interval of sampling to support Figures 2,3,4,5,6,7 and 8.
C. Data in ppm should be submitted at each interval of sampling to support figures 2,3,4,5,6,7 and 8.
D. In most soils about 50% of the residues accounted for are bound.
E. Dissipation was slower in sterile soil.
F. Some $^{14}CO_2$ is given off. Cleavage of the ring is thus noted.
G. Breakdown to pyridinol which appears to buildup. This is in the extractable residues and appear to be the greatest in highly alkaline silt soil. (consistent with faster breakdown at pH increase & alkalinity increases). Organophosphate are unstable in base)

2. Sterilized vs non sterile soil. Ref. 6. chehalis clay loam.

Weeks	% Degraded Autoclaved	Irradicated	Non-sterile.
4	33%	38%	62%

Conclusion

1. Microorganism appeared to speed up degradations, but hydrolysis may be the most important factor.

3. Hydrolytic Stability - Ref. 22 and 27

0.1 ppm added to samples, kept in darkness. Percent remaining in time.

Hours	10°C	24°C	38°C	25°C $pH_{7.7}$
0	100%	100%	100%	100%
8	84%	83%	41.5%	
16	86.9%	73.3%	21.5%	90%
40				41.3%

Conclusion

a. Higher temperature does influence the rate of degradation or volatilization. Volitalized material was not accounted for in this study.
b. No material balance.

4. Effects of Water quality, temperature and light on stability.

a. Faster degradation in pasture water under field conditions.
b. Higher temperature faster the degradation.

5. Effects on microflora of a submerged soil. - Ref. 28
Welimada Clay Loam - Rice crop. pH 5.35, OM 3.22%. 5cm water above soil surface, 27°C, in darkness for 4 weeks prior to addition of Dursban at 1-8 l/A. Soil and water in jars.

Organism and Dursban effect:
Fungi - no effect
Actimomycetes - stimulatory effect
Aerobic Bacteria - stimulatory effect up to 3 months
Ammonifurs - stimulatory effect up to 3 months
Ammonium oxidizer - Suppression. Increased after 3 months.
Nitrite oxidizer - Depression Recovered after 3 months.
Dinitrifiers - Slightly decreased
Aerobic N fixers (non-symbiotic - no effect
Anaerobic N fixers (non-symbiotic - increased
Aerobic P dissolvers - slight inhibition. Increased after 3 months.
Anerobic P dissolvers - Increase in numbers.
Sulfate reducers - Increase in numbers.
Anaerobic cellulose decomposers - Increase in numbers.
Heterotrophic iron precipitators - Stimulatory effect.
Algal population - Increased - Also exposed to light.

Ref. 11 - Inactivating Effects of Microorganisms on Insecticidal Activity of Dursban.

27 species of bacteria did not reduce Dursban. There were 32 colonies of bacteria in peptone and glucose - peptone media.

Conclusion

a. Microbes appear to have little effect on degradation of Dursban.

6. Decomposition and Leaching - Ref. 37 - ^{36}Cl study.

Dursban decomposed slowly in warm, moist soil. About50% remained after 10 weeks. Pyridinol and NaCl were identified as degradation products. Resistant to leaching or movement by water. One study added Dursban to corn cobs. Only 4.5% could be removed or extracted from corn cobs with water. Corn cobs was mixed with soil and placed on Kawkawlin sandy loam (ph_7). 3 inch column. Soil column was eluted. Only 6% was found in leachate.

Conclusion

a. This corn cob study is poor.

1. If only 4.6% could be extracted in water how could one expect any leaching when corn cobs were added to soil columns. 6% did leach. The review is stunned. This study is not acceptable for a leaching study.

7. Leaching and Persistence - Ref. 21.
Some of the data submitted in this study are listed. Analysis for chlorpyrifos and 3,5,6-trichloro-2-pyridinol (pyridinol).

			PPM Chlorpyrifos			PPM Pyridinol		
Lbs/A	g/A	PHI	0-6"	6-12"	12-18"	0-6"	6-12"	12-18"
1 ulv	.5	0	4			.59		
Seed furrow		34	.84	.01	.01	.08	.63	ND
40" row								
		Data at 69, 130 and 365 days <0.05 ppm						
3	0	3.4				1.9		
Band		34	.37	.01	.21	.09	ND	.1
		69	.47	ND	ND	.82	ND	ND

Data at 130 and 365 days 0.01 ppm. The above was on Drummer silty clay loam, pH6, OM 5-6%. Soil plowed.

Lbs/A	g/A	PHI	0-6"	6-12"	12-18"	0-6"	6-12"	12-18"
1 ulv	.5	0	5.5			1.9		
		30	2.2	.23	.1	.04	.27	.1
		77	1.6	.07	.04	1.4	.21	.06
		126	.29	.06	.03	.49	.13	ND
		364	.64	.03	ND	1.8	.08	.05
3		0	9.0			6.3		
		30	4.7	1.8	.83	6.3	1.2	.32
		77	4	.28	.28	4.4	.54	.39
		126	.84	.03	.01	2.3	.2	.07
		364	.56	.06	.02	2.2	.18	.05

The above was on Hastings Silt Loam. pH6, OM 3.5%.

Conclusion

a. Leaching did occur in silt loam.
b. Persistence was also noted in that residues would be available for rotational crops and 1 year later. Possible accumulated from yearly applications.
c. Pyridinol found.

Leaching and persistence and degradation. Ref 20 Application to soil under turkey pens.

		PPM Dursban		Oxygen Ana.		Pyridinol	
Lbs/A	PHI	0-3"	3-6"	0-3"	3-6"	0-3"	3-6"
4	1	.8	.01	0	ND	1.21	.07
	7	.77	.02	0	ND	.73	.05
	28	.87	.01	0	ND	1.72	.08

Soil Hard clay loam.

		PPM Dursban		Oxygen Ana.		Pyridinol	
Lb/A	PHI	0-.25	.25-6	0-.25	.25-6	0-.25	.25-6
4	1	18.4	.01	0	0	1.4	ND
	28	23.2	.03	0	0	6.8	.05
	42	16.8	.01	0	0	1.1	.05
	164	1.4	ND	0	0	8.1	ND

Soil Edwards plateau clay.

Conclusions

a. No oxygen analog could be found in soil. Pyrindinol as expected was found. or
b. Little ~~are~~ no leaching.
c. Persistence is noted.

5

Leaching and persistence - Ref. 5 - Application to soil under turkey pens.

Lbs A/A	Wks. PHI	PPM Dursban 0-3	3-6
4	5	2.76	.04
	8	2.73	.06
	16	.42	.04

Conclusion

a. No leaching noted.
b. No oxygen analog found.
c. Persistence noted.

8. Basic Studies - Ref. 29 - 2,6-^{14}C and ^{36}Cl studies. Volatility studies. Loss of plant surface was 70-80% in 4 hours. Stability to UV. Photodegrades when moisture is present. Chlorpyrifos undergoes hydrolysis to pyridinol which undergoes photodegradation.

9. Photodegradation - Ref. 31 - 2,6-^{14}C study - Photodecomposition in the aerodynamotron. 0.05 ppm added, RH-98-99%, 100°F, 0.5 MPH wind, 24 hrs. exposure. Sunlamps IR40 with wave lengths greater than 300 nm as all lower wave lengths were filtered off. Chlorpyrifos is degraded to dehalogenated and oxidized products of pyridinol and CO_2. Diols, triols and tetraols formed proves that ring cleavage did occur by CO_2 given off.

At the end of 24 hours

	% found
pyridinol	1.33
dehalogenated oxidized products	93.60
CO_2	3.70
Chlorpyrifos	1.0

TLC revealed 5 degradation products.

10. Mosquito control. Air app. Residues in water, soil-silt and oysters. Ref. 3 - 100 A in Miss. was treated with 0.05 lb A/A by air app. (10 lb/A of 0.5%). Soil sampled to 1" to 1.5" deep.

	PPM 1 Hr	2 Hrs.	72Hrs.	7 days	14 days
Water	.001			.0001	
Silt			.007		
Bank near canal	1.216				.226
Bank near artiscan well	.1				.05
Oysters		.007			

Residue, even though not high with time do show up.

11. Biological effects and persistence in freshwater ponds - Ref. 13. Pond near Bakersfield California 30 x 60" area. 27 x 55" water surface. Application 4 times at 2 week intervals at rates of 0.01, 0.05, 0.1 and 1 lb/A

Duckling mortality was 42%. Mosquito fish mortality 10% Zooplankton markedly affected but recovered after 2 weeks. Almost all residues found in to 2"₁ of mud and .1 ppm in bottom 2".

Lbs/A	PHI	PPM Found H_2O	2" Mud	Vegetation	Caged Mosquito fish
.05	4 hrs	.01	ND	.438	3.75
	1 day	.004	.01	.388	1.91
	2 days	.004	.01		1.68
	7 days	ND	.01	.006	1.68
	14 days	ND	.01	.006	.19
1.0	4 hrs	.227	.01	24.38	58
	1 day	.097	.11	42.298	
	7 days	.006	.52	1.85	
0.1	4 hrs			6.36	4.45
	1 day			.224	6.08
	2 days				2.72
	7 days			.23	1.08

Conclusion

a. Very little residue found in water and in 2" level mud.
b. Residues high in vegetation and fish but decrease with time.

12. Fish residue study - Ref. 19-Bluegill study and Bass study.

	.01 Exposure		.05 Exposure	
	PPM Whole Body Residue			
PHI	Bluegill	Bass	Bluegill	Bass
1	.36	.47	1.58	2.08
3	.34	.41	2.06	2.55
7	.20	.23	2.12	.99
14	.04	.21	.17	
28				
Second App.				
35	.42	.27	3.82	1.15
37	.08	.08	2.68	1.32
49	.02	.02	.18	.01
63			.01	.01

Conclusion

a. Fish pick up or accumulate residues but metabolism and ~~excreted~~ elimination eliminate the residues.
b. Experimental protocol not given.
c. Data not on viscera and tissue. This is in another study.

13. Metabolism in Fish - Ref. 32 - 2,6-^{14}C study. Fish exposed to 50 ppb.

Exposure Hours	Tissue	Residues in M Moles/kg Head	Viscera	Skin	Meat
1	.007	.007	.084	.004	.003
4	.028	.002	.061	.0014	.001
8	.047	.001	.058	.001	.001
48	.076	.001	.008	.0015	.0001
144	.004	.0003	.033	.0004	.0002

Conclusion

a. Rapid accumulation in 8-10 hours followed by decrease in residues.

Same study with plants, soil and fish

Hours	Water	Soil Plants	Fish
0	100%		
10	18	59	25
50	35	38	23
80	41	36	22
120	45	38	27

Conclusion

a. Residues in fish increase and then eliminated thus increasing residues in water and in plants.

14. Salt March Habitat Study - Ref. 17 - Air application.

Lb/A	PHI	PPM Found Water	Silt	Oysters
.05	1 hr.	.0082		
	1 day	.0008		.042
	2 days	.0002		.006
	7 days	.0002	.005	.005

Conclusion

a. All samples taken in different areas of application to pond. It would have been better if we had completed results in the same area of sampling.

15. Dursban dripping into flowing water by drip method for irrigation. Ref 25 - Rate 0.1 ppm (1/2 mile long). Found 0.1 to 0.11 ppm in water coming out at the valve. At 100 ft. 0.08 ppm at 10th day and 2" soil 0.04 ppm. At 2000 ft. 0.01 ppm.

16. Persistence and biological activity to 1st Instar cricket nymphs. Ref. 7 - Sandy loam - activity 2-4 wks. - Muck - activity 2-4 wks.

17. Stability in dipping vats - Ref. 39. Stable up to 6 months of testing.

18. Lab testing soil. - Ref. 40. Dursban is bound very tightly to particles of soil and organic matter. Only slight volatilization from, soil and almost no leaching.

19. Soil extracts - Ref. 32 - Soil - Kawkawlin sandy loam pH7.0 100 ppm added.

Week	% Extracted		
Initial	H_2O	MeOH	Acetone
	6.9	86.1	7
1	10.6	82	7.4
2	14.1	78	7.8
4	25.0	69.2	5.8
6	30.3	64.6	5.1
10	37.3	54.4	8

Conclusion

MeOH removes most of the residues in soil at earlier time intervals up to 2 weeks then H_2O and acetone. After 2 weeks water extracts larger amounts of residues. Acetone is a poor extraction solvent. The best extraction solvent appear to be a mixture of H_2O and MeOH.

20. Analytical Method Soil. Chlorpyrifos and its oxygen analog. Ref. 5. Extract with methylene chloride, concentrate, take up in hexane, pass through silicic acid column. Chlorpyrifos and it's oxygen analog may be eluted separately from column. Determine by GC with hydrogen flame detector modified for thermionic detector by use of cesium bromide.

21. Animal studies - Note residues are fat soluble.

    a. Rat - Intubation single dose (^{36}Cl), at 26 hours. 90% in urine, 10% in feces. Oral single dose (2,6-^{14}C), at 72 hours. 68-70% in urine, 14-15% in feces, .15 - .39 as $^{14}CO_2$, 3% in blood and 1.6-1.8% in tissue.
    b. Turkeys - Residues in fat, kidney and liver.
    c. Chickens - Chlorpyrifos in fat, pyridinol in liver and kidney.
    d. Cow - Oxygen analog in cream of molk. Pyridinol in omental renal and subcutaneous fat and muscle.
    e. Swine - Residues in fat, liver and kidney.

RECOMMENDATION

A. RL Registration.

B. The following information are needed:

1. To support D-29, Reference 38, we need data in ppm at each sampling interval for figures 2,3,4,5,6,7 and 8.

2. Leaching studies are needed as defined in the Draft Guidelines.

3. Residue data are needed on rotational crops such as a root crop and soybeans. This is to a labeled study were ^{14}C chlorpyrifos is aged in soil for 120 days then soil is planted to rotational crops. See Draft Guidelines for guidance.

4. A material balance study is needed on hydrolysis. This should be at a pH and temperature were rapid hydrolysis is expected. (pH 7, 7 38°C)

5. A translation of report in Ref. 23 is needed.

Note: The 1/2 life of parent, degradation products and bound residues in over 30 weeks in soils tested. The 1/2 life of extractable residues is less. A crop rotation restriction is needed.

Do not plant subsequent crops within 1 year after treatment 12517 for added to label 46+44