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Date Out EFB: MAR 25 1980

To: Product Manager Jacoby (21)
TS-767

Through: Dr. Gunter Zweig, Chief
Environmental Fate Branch

From: Review Section No. 1
Environmental Fate Branch

Attached please find the environmental fate review of:

Reg./File No.: 7969-LG, 9F2205

Chemical: 3-(3,5-dichlorophenyl)-5-ethenyl-5-methyl-1,3-oxazolidine-
2,4-dione (BAS 352, Ronilan)

Type Product:

Product Name:

Company Name: BAS Wyandotte Corporation

Submission Purpose: use on strawberrries

ZBB Code: Sec. 3

Date in: 5/21/79

Date Completed MAR 25 1980

Deferrals To:

☐ Ecological Effects Branch

☐ Residue Chemistry Branch

☐ Toxicology Branch

1. INTRODUCTION

1.1 This is the first submission for registration of vinclozolin, the proposed common name for the active ingredient in the fungicide RONILAN (50 W).

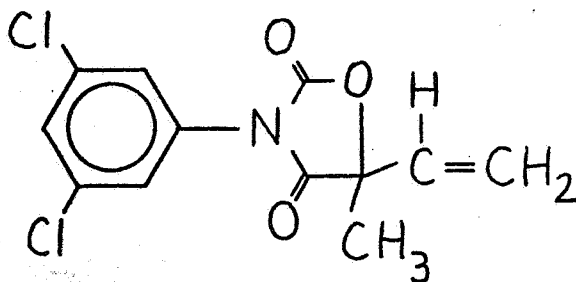
1.2 EFB has reviewed this chemical for EUP's on strawberries (8G2068, April 23, 1978) and lettuce and stone fruits (7969-EUP-RG, August 1, 1979)

1.3 The proposed use is on strawberries.

1.4 Properties

Color - white solid
Odor - characteristic of aromatic compounds
MP - 108°C
Density - 1.5 kg/liter
Solubility (g/100 g solvent)
 water - <0.1
 ethanol - 1.4
 acetone - 43.5
 ethylacetate - 25.3
 cyclohexane - 0.9
 ether - 6.3
 benzene - 14.6
 chloroform - 31.9
Vapor pressure - $<0.1 \times 10^{-6}$ mbar at 20°C .

1.5 Structure



1.6 Vinclozolin is also known as BAS 352 F.

2. DIRECTIONS FOR USE

2.1 Strawberries - Coverage of the developing fruit is essential. The first application should be made not later than 10% primary bloom at the broadcast rates below. The interval between subsequent applications will vary according to weather conditions and resultant disease pressure. If continuous wet periods occur (periods lasting more than 24 hours), immediate retreatment is recommended. Then resume the recommended spray schedule.

<u>Moisture Conditions</u>	<u>Spray Interval (Days)</u>	<u>1st Year Plants or Sparse Foliage, rate</u>	<u>Dense Foliage, rate</u>
All areas except Fla: frequent natural moisture (rain, fog, dew) or when using sprinkler irrigation (high disease pressure)	7-9	0.5 lb. ai/A	0.75-1.0 lb. ai/A
Limited natural moisture, infrequent sprinkler irrigation (low disease pressure)	10-14	0.5 lb. ai/A	0.75-1.0 lb. ai/A
In Fla. (winter pro- duction)	3-5	0.5 lb. ai/A	0.75-1.0 lb. ai/A

Apply in at least 100 gallons of spray solution per acre to obtain thorough coverage of developing fruit. Do not apply more than 17.5 pounds of active ingredient per acre per season. Do not apply during rain.

2.2 There is no disposal information on the submitted label.

3. DISCUSSION OF DATA

3.1 Investigations into the Hydrolysis Stability of Vinclozolin as a Function of pH Value and Temperature, Dr. S. Otto, Report No. 1504, January 23, 1978, Acc. No. 096967, tab J-2.

Procedure

U-Phenyl-¹⁴C-labeled vinclozolin in buffered solutions of pH 3, 6 and 9 at concentrations of 0.18 and 1.8 ppm vinclozolin was monitored for hydrolysis.

Method of analysis

Samples (except from the pH = 3 run) were acidified to pH 3-5, extracted with ethyl acetate and aliquots were taken for measurement of radioactivity and analysis by TLC.

Results

1.	<u>pH</u>	<u>fortification</u>	<u>temperature</u>	<u>halflife</u>
	9	1.78 ppm	25°C	12.6 min.
			35	4.8 min.
			45	1.6 min.
	9	.178 ppm	25°C	15.4 min.
			35	5 min.
			45	1.4 min.
	6	1.78 ppm	25°C	61 hr.
			35	22.5 hr.
			45	9.5 hr.
	6	.178 ppm	25°C	49 hr.
			35	22 hr.
			45	10.5 hr.
	3	1.78 ppm	25°C	70 hr. days
			35	22.5 hr. "
			45	12 hr. "
	3	.178 ppm	25°C	70 hr. days
			35	24.5 hr. "
			45	12 hr. "

2. At pH 6 and 9, 3,5-dichlorophenylcarbamic acid (1-carboxy-1-methyl) allyl ester, known as metabolite B, and N-(3,5-dichlorophenyl)-2-hydroxy-2-methyl-3-butenic acid amide, known as metabolite E, form, with 2-5 times more B forming than E.

At pH 3, E is the major product with B not exceeding 4%.

The material balance is ^{maintained} ~~mentioned~~ with the parent vinclozolin and metabolites B and E, during hydrolysis.

Conclusions

Vinclozolin hydrolyzes with the shortest halflives at alkaline pH's and higher temperatures. At 25°C and pH's of 9, 6 and 3, halflives of 12 minutes, 61 hours and 70 days, respectively, are expected. Two hydrolysis products form. One is N-(3,5-dichlorophenyl)-2-hydroxy-2-methyl-

←

4

3-butenic acid amide, which forms at all pH's, but after 5 days does not reach 30% of the initial amount except at pH 3 at temperatures greater than 35°C. The other product is 3,5-dichlorophenyl-carbamic acid (1-carboxy-1-methyl) allyl ester which forms at all pH's and after 5 days will represent at least 57% of the initial amount except at pH 3 when it does not exceed 4%.

3.2 Photolysis of ¹⁴C-Vinclozolin on Soil, Huber, R. and Otto, S., Lab Communication No. 829, January 1979, Acc. No. 098255, tab J-2.

Procedure

A loamy sand with 1% moisture (Neuhofen soil) was fortified at 7.8 ppm with phenyl-U-¹⁴C-vinclozolin and exposed to about 40,000 lux from a sunlamp with radiation greater than 280 nm. The soil temperature did not exceed 25°C.

Method of analysis

Soil samples were extracted with methanol followed by 1% methanolic HCl with partitioning into n-hexane and ethylacetate. The fractions were analyzed by LSC, TLC, HPLC and GC/MS.

Results

Days	1) <u>Distribution of Radioactivity</u>	
	<u>Methanol extract</u>	<u>Residual Soil</u>
0	7.80 (100%)	
1	6.49 (83%)	0.52 (7%)
3	6.43 (82%)	0.75 (10%)
18	4.10 (53%)	2.28 (29%)

2) <u>Partitioning of Day 18 Methanolic HCl Extract (ppm)</u>			
<u>Methanolic HCl Extract</u>	<u>n-Hexane phase</u>	<u>Ethylacetate phase</u>	<u>Aqueous phase</u>
2.87 (37%)	1.25 (16%)	0.54 (7%)	0.68 (9%)

3) The methanol extract contained only parent vinclozolin as did the n-hexane phase. The ethylacetate phase contained parent compound, N-(3,5-dichlorophenyl)-2-hydroxy-2-methyl-3-butenic acid amide known as metabolite E and 3-(3,5-dichlorophenyl)-5-methyl-1,3-oxazolidine-2,4-dione known as metabolite S. Another photoproduct was found and was tentatively identified as 3-(3,5-dichlorophenyl)-5-(1-hydroxyethyl)-5-methyl-2,4-oxazolidine dione known as photoproduct W.

Conclusions

Vinclozolin will photolyze on soil with a half-life of 19 days. Three photoproducts form, metabolite E, metabolite S and photoproduct W (proposed). (For chemical names and structures see results 3) above and section 3.26, below.

3.3 Sensitized Photolysis of ^{14}C -Vinclozolin in Water, Drs. Huber, Beutel, Ohnsorge, Report No. 1599, November 1978, Acc. No. 098255, tab J-1.

Procedure

^{14}C - Phenyl ring labeled vinclozolin was added to distilled water adjusted to pH 2-3 with conc. H_2SO_4 (to prevent hydrolysis), resulting in a 1.83% acetone in water solution fortified to 2.02 ppm vinclozolin.

The solution was exposed to artificial sunlight (280 nm-cutoff) and a stream of air carried any volatiles through 0.1 N sulfuric acid and scintillation cocktail traps.

During 5 hours of irradiation, samples were also withdrawn from the vinclozolin solution and the temperature was kept at $20 \pm 2^\circ\text{C}$.

Method of analysis

The gas traps and the different extracted fractions of the irradiated solution were analyzed by HPLC, TLC, GC-MS and standard LSC techniques.

Results

1) After 5 hours irradiation, the sulfuric acid traps showed no activity and the scintillation cocktail trap showed 0.2% of the applied activity.

2) The half-life of the parent vinclozolin was found to be 3.6-3.8 hours.

3) After 5 hours irradiation, the activity in the irradiated solution partitioned 53% in ethyl acetate, 45% in n-hexane and 2% in water. The ethyl acetate fraction contained a major product, 3-(3,5-dichlorophenyl)-5-formyl-5-methyl-1,3-oxazolidine-2,4-dione, known as formyl derivative U, at 40% of the initial activity and the following 2 products representing a combined total of 5% of the initial activity: 3,5-dichlorophenyl isocyanate and 3,5-dichloropyruvic acid anilide. Also, the n-hexane fraction contained 3-(3,5-dichlorophenyl)-5-oxiranyl-5-methyl-1,3-oxazolidine-2,4-dione, known as epoxide V, and is the probable precursor to formyl derivative U. After 5 hours irradiation, epoxide V represented 4% of the initial activity.

- 4) The 3,5-dichloraniline moiety remained intact during the experiment.
- 5) The registrant states (with no supporting data) that cold vinclozolin did not photolyze after 30 days irradiation.
- 6) The control showed no degradation of the parent compound.

Conclusions

Vinclozolin is stable to aqueous photolysis but will photolyze under sensitized aqueous photolysis at 20°C with a halflife of 3.5-4 hours. The major degradation product is 3-(3,5-dichlorophenyl)-5-formyl-5-methyl 1,3-oxazolidine-2,4-dione (40% after 5 hours) with minor amounts (<5 %) of the following also forming: 3-(3,5-dichlorophenyl)-5-oxiranyl-5-methyl 1,3-oxazolidine-2,4-dione which is the probable precursor of the major degradation product, 3,5-dichlorophenyl isocyanate and 3,5-dichloropyruvic acid anilide.

Degradation of the 3,5-dichloroaniline moiety is not expected under aqueous photolysis.

3.4 Further Investigations into the Aerobic Soil Metabolism of BAS 352 F-14C (¹⁴C-Vinclozolin), Huber, R., Otto, S., No. 1571, September 1978, Acc. No. 098255, tab J-6.

Procedure

A Neuhofen soil (loamy sand, 83% sand, 7% silt, 10% clay, 2.6% organic carbon, pH = 6.8, CEC = 10, bulk density = 1.4, moisture capacity = 39.3%) and a Pfungstadt soil (loam, 68% sand, 18% silt, 16% clay, 0.7% organic carbon, pH = 7.4, CEC = 13, bulk density = 1.3, moisture capacity = 33.3%) were fortified to 7 ppm with vinclozolin labeled in either one of the following 2 places, (1) phenyl-U-¹⁴C or (2) 5-¹⁴C, and incubated for 120 days with periodic sampling. The soil temperature was maintained at 20 or 25°C and moisture content was kept at 40%.

Method of analysis

Soil aliquots were taken for combustion and for extraction with analysis of the different fractions by LSC, TLC, LC, HPLC and GC/MS techniques.

Results (for names of 5, E, D and B, see results 4, below)

1) Balance of BAS 352 F-(phenyl-U-¹⁴C) and metabolites in Neuhofer soil (loamy sand) and various fractions; Temp. 25 + 2 °C.

days	total radio-activity	Methanol-Extr.	Soil Residue	Ethylacetate/H ₂ O partition Ethyl- acetate phase	Values (ppm) after HPLC of EtOAc phase	S	E	D	B
0	7.68	7.34	0.08	7.47	0.01	7.10	0.23	0.04	0.13
7	7.50	6.73	0.62	6.95	0.02	6.07	0.18	0.13	0.51
14	7.60	6.37	1.12	6.44	0.04	5.25	0.17	0.14	0.73
60	7.41	3.74	3.62	3.75	0.05	2.22	0.11	0.06	0.94
90	7.56	2.65	4.27	2.69	0.07	1.45	0.10	0.06	0.37
120	7.65	1.94	4.71	2.06	0.04	0.95	0.11	0.05	0.46

All values in ppm of BAS 352 F equivalents

2) Balance of BAS 352 F-(5-¹⁴C) and metabolites in Neuhofen
soil (loamy sand) Temperature at 20 + 2 °C.

days (20°C)	total radio- activity	Methanol-Extr. Extr.	Soil Residue	Ethyl- partition acetate phase	Ethylacetate/H ₂ O Water phase	HPLC of EtoAc phase (ppm) BAS 352 F B	S	E
0	6.84	7.15	0.06	7.38	0.01	6.73	0.60	--
7	7.45	6.77	0.59	6.77	0.01	5.46	0.66	0.10
14	7.20	6.33	1.03	6.29	0.04	4.97	0.55	0.09
30	7.40	5.50	1.55	5.39	0.03	3.98	0.44	0.09
60	5.68	3.69	2.38	3.59	0.05	2.61	0.28	0.04
90	5.31	2.03	2.70	2.43	0.06	1.74	0.20	0.04
120	4.81	1.98	2.51	1.89	0.07	1.39	0.15	--
(25°C)								
0	7.32	7.55	0.07	7.31	0.01	6.68	0.53	0.04
7	7.31	6.19	0.71	6.48	0.03	5.35	0.62	0.12
14	7.30	5.65	1.26	5.54	0.06	4.29	0.60	0.11
30	6.61	4.25	1.93	4.09	0.07	2.90	0.30	0.08
60	5.75	2.59	2.45	2.45	0.06	1.49	0.15	0.03
90	4.91	2.01	2.78	1.84	0.07	1.09	0.08	0.02
120	4.07	1.06	2.53	0.94	0.07	0.61	0.04	--

All values in ppm of BAS 352 F equivalents.

9

3) Balance of BAS 352 F-(phenyl-U-¹⁴C) and metabolites in
Pfungstadt soil (loam) Temperature at 20+2°C and
25 + 2 °C

days (20°C)	total radio- activity	Methanol-Extr.	Residue	Ethylacetate/H ₂ O		HPLC of EtOAc phase (ppm)			D	B
		Extr.		Soil	partition	water	BAS 352F	S		
				Ethylacetate phase	water phase					
0	6.65	6.79	0.14	6.92	0.02	6.37	0.23	0.09	0.04	0.20
7	6.74	5.69	1.20	5.57	0.08	2.37	0.42	0.55	0.08	2.15
14	7.08	5.09	1.55	5.17	0.13	1.60	0.09	0.55	0.14	2.79
30	6.51	4.66	2.05	4.54	0.12	0.97	0.21	0.44	0.29	2.63
60	6.66	3.81	3.38	3.85	0.07	0.57	0.12	0.16	0.43	2.58
90	6.59	3.19	3.50	3.12	0.07	0.43	0.11	0.09	0.51	1.98
120	6.57	2.43	4.07	2.19	0.15	0.33	0.09	0.07	0.38	1.31
(25°C)										
0	6.51	6.72	0.08	7.00	0.01	6.03	0.65	0.10	0.04	0.18
7	6.60	4.73	1.90	4.89	0.12	1.56	0.15	0.56	0.19	2.42
14	6.70	4.50	2.09	4.43	0.23	1.01	0.08	0.40	0.17	2.77
30	6.98	3.40	2.28	3.38	0.13	0.57	0.08	0.14	0.22	2.38
60	6.83	2.21	4.48	2.12	0.15	0.33	0.07	0.07	0.24	1.41
90	6.72	1.70	4.78	1.68	0.09	0.27	0.07	0.07	0.28	0.99
120	6.42	1.15	5.23	1.14	0.09	0.23	0.06	0.06	0.13	0.66

All values in ppm 352 F equivalents.

- 4) BAS 352 F is vinclozolin (parent compound)
metabolite S is 3-(3,5-dichlorophenyl)-5-methyl-1,3-
oxazolidine-2,4-dione
metabolite E is N-(3,5-dichlorophenyl)-2-hydroxy-2-methyl-3-
butenoic acid amide
metabolite D is 3,5-dichloroaniline
metabolite B is 3,5-dichlorophenylcarbamic acid (1-carboxy-1-
methyl)-2-propenyl ester

Conclusions

1) Vinclozolin degrades in soil under aerobic conditions. The half-life in a loamy sand of pH 6.8 is 3-7 weeks at 20-25°C and the half-life in a loam of pH 7.4 is 3-4 days at 20-25°C. This is in agreement with the hydrolysis data (see section 3.1, above) which shows vinclozolin to be least stable at alkaline pH's.

2) The loss of ^{14}C activity shown in the 5 - ^{14}C labeled studies is due to cleavage of the heterocyclic ring with release of $^{14}\text{CO}_2$. This indicates soil microbes contribute to the aerobic soil degradation of vinclozolin.

3) Four soil metabolites form; S, which is 3-(3,5-dichlorophenyl)-5-methyl-1,3-oxazolidine-2,4-dione, E which is N-(3,5-dichlorophenyl)-2-hydroxy-2-methyl-3-butenic acid amide, D, which is 3,5-dichloroaniline and B, which is 3,5-dichlorophenylcarbamic acid (1-carboxy-1-methyl) allyl ester. Metabolites S and E peak at 2-8% of initial vinclozolin concentration after 2 weeks aerobic soil incubation and then steadily decline to about 1/10 of the peak value by day 120 of incubation. Metabolite D peaks at 4-10% of initial vinclozolin concentration at 90 days and declines to 50-80% of the peak value by day 120. Metabolite B peaks at 12-40% of the initial concentration after 2-4 weeks at steadily declines to 1/4-1/2 the peak value by day 120.

3.5 Degradation of ^{14}C -Vinclozolin (BAS 352 F) in Soil under Aerobic, Anaerobic and Sterile Conditions, Hamm, R., October 1978, Report No. 1592, Acc. No. 098255, tab J-7.

Procedure

Neuhofen soil (loamy sand, 10.1% silt and clay <20 μ , 2.58% organic carbon, pH 6.8, bulk density = 1.4, CEC = 10) was fortified to about 9 ppm with U- ^{14}C -phenyl-vinclozolin and then adjusted to 40% moisture capacity. The flask was wrapped light proof and incubated aerobically at $20 \pm 1^\circ\text{C}$.

An anaerobic flask was similarly prepared except for flooding with water and flushing with nitrogen. A sterile flask was also similarly prepared except for autoclaving of the soil before fortification with vinclozolin.

Incubation was for 60 days and moisture content was maintained. The soil was also microbiologically examined.

Method of analysis

The soil was sampled and extracted with methanol followed by LSC and TLC analysis of aliquots of the methanol extract.

Results

1. Methanol Extractable ^{14}C from Moist Soil (ppm)

<u>Day of Incubation</u>	<u>Conditions</u>		<u>Sterile/Aerobic</u>
	<u>Aerobic</u>	<u>Anaerobic</u>	
3	9.14	NS	9.19
7	9.00	NS	9.13
14	9.21	NS	9.00
21	8.50	NS	8.70
28	7.66	8.03	8.16
60	6.25	7.80	8.14

NS= no sampling

2. Metabolites B, D and E appear in different amounts under all soil conditions tested during the 60 day course of the experiment. Quantitative results were not provided.

3. Populations of soil bacteria, actinomycetes and fungi were not altered during the experiment.

Conclusions

1. Soil degradation of vinclozolin is greatest under aerobic conditions, is relatively moderate under anaerobic conditions and occurs relatively slowly under sterile/aerobic conditions. Degradation of vinclozolin in soil is due to both microbial and chemical action.

3.6 Investigations on the Microbial Metabolism of ^{14}C -Vinclozolin
(BAS 352 F), Hamm, R., Laboratory Report No. 1595, October 1978, acc # 098255, tab J-8.

Procedure

Soil microbes that could utilize vinclozolin as the sole carbon source were isolated from Limburgerhof soil (loamy sand, 16% particles <20 μ , 1.05% organic carbon, pH in KCl= 7.1, CEC= 7) and identified as:

1. *Bacillus licheniformis*
2. *Bacillus megaterium*
3. unbekannter Phialidenpilz
4. *Actinomucor elegans*
5. *Phialophora* cf. *cyclaminis*
6. *Actinomyces* spec.
7. *Strep. violaceoruber*
8. *Strep. violaceus*

These organisms plus the following pure strains of soil microbes:

1. *Altenaria alternata* CBS 105.24
2. *Ankistrodesmus braunii* ATCC 12744
3. *Bacillus sphaericus* ATCC 12123
4. *Botrytis cinerea* CBS 121.39
5. *Penicillium chrysogenum* CBS 194.46
6. *Streptomyces rimosus* ATCC 19656

were exposed to an unknown concentration of ^{14}C -vinclozolin in an 0.1% glucose nutrient solution for 35 days.

Method of analysis

Samples of the nutrient medium were periodically taken during incubation and extracted with ethyl acetate. The extract was concentrated and analyzed by TLC.

Results

Metabolites B, E and D were found in all batches including the control; the only difference being in concentration. (See section 3.26, below for chemical names and structures.)

Conclusions

Soil microbes can degrade vinclozolin. How much soil microbes contribute to the degradation of vinclozolin cannot be determined from the data since vinclozolin also degraded in the control flask. The vinclozolin was also subjected to different pH environments in the nutrient media due to microbial metabolism and vinclozolin readily degrades in alkaline media.

3.7 Investigations on the Influence of Vinclozolin on Various Soil Microorganisms, Hamm, R., Report No. 1598, November 1978, acc # 098255, tab J-9.

Procedure

The effect of vinclozolin at 10 ppm on the following soil microbial enzymatic reactions was determined:

<u>Enzyme</u>	<u>Substrate</u>	<u>Microbe</u>	<u>Testing method</u>
Amylase	Amylose	Pseudomonas aeruginosa Aspergillus niger	Determining glucose via hexokinase method
Cellulase	Cellulose	Cellulomonas Trichoderma viride	Hexokinase method
Proteinase	Albumin	Trichoderma viride	Biuret reaction
Pectinase	Pectin	Fusarium oxysporum	Decreasing viscosity of pectin

Also, the effect on the growth rate of Chlorella of 10 ppm vinclozolin in nutrient solution was determined using a counting chamber after growth for 7 days under 4,000 Lux at 25° C and the growth rate of blue algae Nostoc muscorum was evaluated by monitoring color intensity and by wet and dry weights of the biomass as compared to the control. Finally, soil respiration of Neuhofen soil fortified at 10 ppm vinclozolin and kept in the dark was determined by monitoring CO₂ evolution.

Results/Conclusions

1. Negative results were exhibited only on Pseudomonas aeruginosa and Nostoc muscorum. However, since P. aeruginosa is not involved in soil fertility but is an opportunist plant and human pathogen, vinclozolin effects on it will not impinge on our review. Growth of N. muscorum was totally inhibited. Since N. muscorum fixes nitrogen, the effect of vinclozolin on other nitrogen fixers should be assessed. Also, will the inhibition of the growth of this algae alter microbial symbiotic relationships relevant to soil fertility?

2. Data on nitrogen fixation and nitrification are needed as are tests measuring enzyme activity for dehydrogenase or phosphatase. Also, to study effects on the degradation of cellulose, starch, pectin and protein at least one each of soil bacteria, actinomycetes and molds must be used. See RECOMMENDATIONS for more detail.

3. The effects of vinclozolin on soil microbes will be assessed after receipt and evaluation of the additional data.

3.3 Soil Leaching of Vinclozolin, Beutel and Huber, Lab
Communication No. 826, October 9, 1978, acc. no. 098255, tab J-10.

Procedure

Leaching of vinclozolin applied at a rate of 0.9 lb ai/A (0.2 mg ai/20 cm²) to 12 inch soil columns of the following 4 soils and eluted with 200 mm of water was determined.

Soil Characteristics

	<u>Lufa soil</u>	<u>Neuhofen soil</u>	<u>Hatzenbühl soil</u>	<u>Pfungstadt soil</u>
Soil type	sand	loamy sand	sandy loam	loam
% sand	95	83	78	66
% silt	1	7	11	18
% clay	4	10	11	16
% organic C	0.5	2.6	1.12	0.7
pH	6.8	6.1	7.1	7.4
bulk density	1.4	1.4	1.13	1.3
CEC	3.7	10	8.6	13

Method of analysis

The eluate was analyzed for 3,5-dichloroaniline containing residues.

Results

<u>Soil type</u>	<u>% of applied ai* found in eluate</u>
sandy	2.5
loamy sand	0
sandy loam	0.2
loam	0

*equivalents

Conclusions

Vinclozolin, as the parent compound, does not leach.

3.9 Experiments on the Leaching of ¹⁴C-Vinclozolin and its Degradation Products after a Degradation Period of 30 Days, Otto, S., Report No. 1464, Sept. 28, 1977, acc. # 098255, tab J-11.

Procedure

Two standard soils, Neuhofen (loamy sand, 83% sand, 2.58% organic carbon, 10.1% particles <20 u, pH= 6.8) and Hatzenbühl (loamy sand, 1.0% organic carbon, 78% sand, 19.5 % particles <20 u, pH=6.2), were fortified to 7 ppm with phenyl-U-¹⁴C-vinclozolin, brought to 40% water capacity and aged aerobically for 30 days at 20°C.

Soil columns were then filled with 5 cm sea sand followed by 20 cm untreated soil and topped off with 10 cm of the fortified, aged soil. The column was saturated with water from the top and then irrigated with 12.5 mm water daily for 45 days.

Method of analysis

The eluate was measured for radioactivity daily. Activity remaining in the soil was determined by combustion.

Results

1. The soil column was divided into 7 segments (presumably of equal size) and analyzed for ^{14}C content.

<u>Segment no. (Neuhofen soil)</u>	<u>% of recovered ^{14}C activity</u>
1	22.3
2	47.6
3	10.9
4	7.6
5	4.1
6	3.9
7	0.5
eluate	3.2

<u>Segment no. (Hatzenbühl soil)</u>	<u>% of recovered ^{14}C activity</u>
1	13.1
2	45.3
3	25.7
4	4.7
5	0.8
6	0.4
7	0.1
eluate	9.9

3. During the first 7 days of leaching, activity in the eluate was primarily vinclozolin, but thereafter was primarily metabolite B which is 3,5-dichlorophenyl-carbamic acid (1-carboxy-1-methyl)-allyl ester.

Conclusions

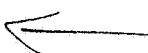
Soil aged residues of vinclozolin leach weakly.

3.10 Determination of the Constants of the Adsorption Isotherm of Vinclozolin in the System Soil/Water, Lab Communication No. 811, November 1978, J. Redeker, acc.# 098256, tab J-16

Procedure

The following 3 soils were used in this adsorption/desorption experiment:

	<u>Soil I</u> <u>Pfungstadt</u>	<u>Soil II</u> <u>Neuhofen</u>	<u>Soil III</u> <u>LUFA</u>
Type	loam	loamy sand	sand
% <20 μ	40	14.9	7.5
pH	7.3	7.2	7.0
CEC	13	10	3.7
org. C	0.58	2.66	0.51
Density	1.30	1.31	1.55

Aliquots of the soils were added to aqueous solutions of ^{14}C -vinclozolin to equilibrate for 2 hours followed by filtration by centrifugation. Desorption was done using distilled water and saturated CaSO_4 solution. 

Aliquots of the filtrate were subjected to LSC to determine ^{14}C content.

Results

<u>Soil</u>	<u>$^{\circ}\text{C}$</u>	<u>K_{ads}</u>	<u>$\frac{1}{n}$</u>	<u>K_{Des}</u>	<u>$\frac{1}{n}$</u>	<u>$K_{\text{Des}} \text{CaSO}_4$</u>	<u>$\frac{1}{n}$</u>
I	30	0.593	0.936				
II	22	9.683	0.915				
	30	8.322	0.921	8.640	0.930	16.66	0.966
III	30	1.383	0.940	4.623	0.987		

Conclusions

The K_{ads} values on soils I and III indicate some leaching may occur beyond the top few inches of soil. The percentage of pesticide adsorbed to soil can be calculated ^{1/} from the following K values:

<u>K</u>	<u>% adsorbed</u>
1	80
2	89
4	94
8	97
20	98.8
50	99.5

^{1/} Goring and Hamaker, Organic Chemicals in the Soil Environment, vol. 1, pg 77-78.

However, the soil column leaching data (in section 3.8, above) indicates less leaching will occur than predicted by this soil adsorption data.

3.11 Determination of BAS 352 F and its 3,5-Dichloroaniline Containing Metabolite Residues in Deep Core Soil Samples, Report No. PR-170, March 17, 1978, acc. # 098255, tab J-12.

Procedure

Strawberry plots in Watsonville, California, in Northwood, North Dakota and in Corvallis, Oregon were treated with vinclozolin 13, 4 and 6 times respectively at rates of 0.5 to 2.0 lb ai/A. Soil cores were sampled to 6 feet and the soil was analyzed for parent compound and 3,5-dichloroaniline containing residues.

Results

1. The California plots, treated at 0.5 and 2.0 lb ai/A 13 times each at 9-18 day intervals, were sampled 28 days after the last treatment to 6 feet. Detectable residues (>0.05 ppm) were found in the top foot only at 0.06-0.1 ppm.

2. The North Dakota plots, treated at 1.0 and 2.0 lb ai/A 4 times each at 2-2 1/2 week intervals, were sampled 144 days after the last treatment to 3 feet. Detectable residues (>0.05 ppm) were found in the top foot only at 0.08-0.22 ppm.

3. The Oregon plots, treated at 1.0 and 2.0 lb ai/A 4-5 times each at 1-2 week intervals were sampled 158 days after the last treatment to 6 feet. Detectable residues (>0.05 ppm) were found in the top foot only at 0.05 ppm.

Conclusions

Vinclozolin is not persistent and its residues do not leach in soils common to the proposed strawberry use. Buildup of residues from yearly use of vinclozolin is not expected.

3.12 Determination of BAS 352 F and its 3,5-Dichloroaniline-Containing Metabolite Residues in Deep Core Soil Samples, Report No. PR-185, April 4, 1979, acc. # 098255, tab J-13.

Procedure

Strawberry plots in Northwood, North Dakota were treated with vinclozolin at 1.0 lb ai/A 1, 2 or 3 times and sampled up to 84 days after the last treatment to a depth of 24 inches. The soil was analyzed for vinclozolin and its 3,5-dichloroaniline containing metabolites.

Results

1) Vinclozolin equivalents in soil resulting from applications of 1.0 lb ai/A to strawberry plots

TREATMENT DATE(S)	SAMPLING DATE(S)	SAMPLING INTERVAL FROM LAST TREATMENT (DAYS)	INTERVAL BETWEEN LAST TWO APPLICATIONS (DAYS)	BAS 352 F EQUIVALENTS FOUND (PPM)	SOIL DEPTH (INCHES)
-	7-17-78	-	-	<0.05	0-6
-	7-17-78	-	-	<0.05	18-24
7-17-78	7-17-78	0	-	0.38	0-6
7-17-78	7-17-78	0	-	0.05	6-12
7-17-78	7-17-78	0	-	<0.05	12-18
7-17-78	7-17-78	0	-	<0.05	18-24
7-17-78	8-2-78	16	-	0.27	0-6
7-17-78	8-2-78	16	-	0.05	6-12
7-17-78	8-2-78	16	-	<0.05	12-18
7-17-78	8-2-78	16	-	<0.05	18-24
7-17-78,8-2-78	8-2-78	0	16	0.41	0-6
7-17-78,8-2-78	8-2-78	0	16	0.13	6-12
7-17-78,8-2-78	8-2-78	0	16	0.05	12-18
7-17-78,8-2-78	8-2-78	0	16	<0.05	18-24
7-17-78,8-2-78	8-7-78	5	16	0.31	0-6
7-17-78,8-2-78	8-7-78	5	16	0.07	6-12
7-17-78,8-2-78	8-7-78	5	16	<0.05	12-18
7-17-78,8-2-78	8-7-78	5	16	<0.05	18-24
7-17,8-2,8-7-78	8-7-78	0	5	0.77	0-6
7-17,8-2,8-7-78	8-7-80	0	5	0.07	6-12
7-17,8-2,8-7-78	8-7-78	0	5	<0.05	12-18
7-17,8-2,8-7-78	8-7-78	0	5	<0.05	18-24
7-17,8-2,8-7-78	8-10-78	3	5	0.62	0-6
7-17,8-2,8-7-78	8-10-78	3	5	0.11	6-12
7-17,8-2,8-7-78	8-10-78	3	5	<0.05	12-18
7-17,8-2,8-7-78	8-10-78	3	5	<0.05	18-24
7-17,8-2,8-7-78	8-14-78	7	5	0.55	0-6
7-17,8-2,8-7-78	8-14-78	7	5	0.12	6-12
7-17,8-2,8-7-78	8-14-78	7	5	<0.05	12-18
7-17,8-2,8-7-78	8-14-78	7	5	<0.05	18-24
7-17,8-2,8-7-78	8-22-78	15	5	0.55	0-6
7-17,8-2,8-7-78	8-22-78	15	5	0.16	6-12
7-17,8-2,8-7-78	8-22-78	15	5	<0.05	12-18
7-17,8-2,8-7-78	8-22-78	15	5	<0.05	18-24
7-17,8-2,8-7-78	9-11-78	35	5	0.25	0-6
7-17,8-2,8-7-78	9-11-78	35	5	0.07	6-12
7-17,8-2,8-7-78	9-11-78	35	5	0.06	12-18
7-17,8-2,8-7-78	9-11-78	35	5	<0.05	18-24
7-17,8-2,8-7-78	10-30-78	84	5	0.19	0-6
7-17,8-2,8-7-78	10-30-78	84	5	<0.05	6-12
7-17,8-2,8-7-78	10-30-78	84	5	<0.05	12-18
7-17,8-2,8-7-78	10-30-78	84	5	<0.05	18-24

Conclusions

The halflife of vinclozolin after single or a group of repeated applications is about a month in strawberry plots of pH 7.6. Leaching of detectable residues beyond 12 inches is not expected.

3.13 Determination of BAS 352 F and its 3,5-Dichloroaniline - Containing Metabolite Residues in Soil and Water Samples from Field Leaching Study, Report No. PR-187, April 4, 1979 acc. # 098255, tab J-14.

Procedure

An 0.09 acre plot feeding one ground tile buried 3 feet deep of a sandy loam soil type (73% sand, 18% clay, 9% silt, pH= 5.6, 0.9% OM) was treated with vinclozolin at 3.0 lb ai/A. Soil and tile water samples were taken over 31 days post-treatment during which time the plot was sprinkle irrigated 5 times with a total of 31.2 inches of water.

Method of analysis

The soil and water samples were analyzed for parent compound and its 3,5-dichloroaniline-containing products. The soil was extracted with acetone:water (9:1) and the water samples were hydrolyzed directly.

Results

1. Vinclozolin and its 3,5-Dichloroaniline-Containing Residues in Soil from Application of 3.0 lb Vinclozolin/Acre on Aug. 29, 1978

<u>Sampling interval (days)</u>	<u>Vinclozolin equivalents (ppm)</u>	<u>Soil Depth (inches)</u>
0	1.11	0-4
2	0.78	0-4
6	0.85	0-4
13	0.55	0-4
30	0.32	0-4
0	0.52	4-8
2	0.12	4-8
6	0.11	4-8
13	0.12	4-8
30	0.07	4-8
0	0.16	8-12
2	0.08	8-12
6	0.05	8-12
13	<0.05	8-12
30	<0.05	8-12
0	0.13	12-24
2	<0.05	12-24
6	<0.05	12-24
13	<0.05	12-24
30	<0.05	12-24

2. Residues were not detected (<0.01 ppm) in the water samples coming off the 3 foot deep ground tile.

Conclusions

1. Combined vinclozolin and its 3,5-dichloroaniline-containing residues dissipate in soil under field conditions with a halflife of 2 weeks. Leaching of residues beyond 3 feet is not evident.

3.14 Addendum to BWC Agricultural Chemicals Method No. 25 for the Determination of BAS 352 F and its 3,5-Dichloroaniline-Containing Metabolites in Water, Analytical Method No. 25 B, March 15, 1979, acc.# 098255, tab J-15.

Procedure

This method is an adaptation of method no. 25 (for soil) to permit analysis of water for vinclozolin and its 3,5-dichloroaniline-containing products. It involves subjecting the residues in the water to direct hydrolysis and analyzing for 3,5-dichloroaniline-containing residues via GC-EC.

The method is sensitive to 0.01 ppm with 85-104% recovery between 0.01-0.05 ppm fortifications.

3.15 Determination of BAS 352 F and its 3,5-Dichloroaniline Containing Metabolite Residues in Soil Samples, submitted by W.E. Horton of BASF, report no. PR-169, Feb. 28, 1978, acc. # 098256, tab J-17.

Procedure

Four soils planted to strawberries in California, North Dakota, Florida, and Mississippi were treated with vinclozolin at rates of 0.25 - 2.0 lb. ai/A between 1 and 22 times at 1/2 to 2 1/2 week intervals. The 3 soils analyzed had a pH of 6.8 - 7.3. One soil had 9.5% OM and the other 2 had 1% OM.

Soil samples were analyzed to 12 inches for parent and 3,5-dichloroaniline-containing metabolites.

Conclusions

Enough sampling was not performed to establish patterns of residue decline. More sampling should have been taken at later treatment intervals. In general, it can be seen, however, that residues build up and persist more after repeated applications than after single applications. Also, with higher rates and more applications, leaching of residues to the 12 inch level becomes more evident.

3.16 Determination of BAS 352 F and its 3,5-Dichloroaniline Containing Metabolite Residues in Soil Samples, submitted by W.E. Horton of BASF, March 17, 1978, report no. PR-169-A, acc. #098256, tab J-18.

Procedure

Three soils planted to strawberries in California, Oregon and North Dakota were treated with vinclozolin at rates of 0.25 - 2.0 lb ai/A between 1 and 12 times at 1/2 to 3 week intervals.

The respective pH and organic matter content (%) of the 3 soils were 7.2 and 1.0, 5.9 and 2.1 and 7.3 and 9.5.

Soil samples were analyzed for vinclozolin and its 3,5-dichloroaniline-containing metabolites to a depth of 12 inches.

Results

1) Residues of vinclozolin equivalents found (California test, 12 treatments)

<u>lb ai/A per treatment</u>	<u>sampling interval from last treatment (days)</u>	<u>vinclozolin equivalents (ppm)</u>	<u>soil depth (inches)</u>
0.5	8	0.34	0-4
		< 0.05	4-8
		< 0.05	8-12
	15	0.42	0-4
		< 0.05	4-8
		< 0.05	8-12
	31	0.27	0-4
		< 0.05	4-8
		< 0.05	8-12
	81	0.16	0-4
		< 0.05	4-8
		< 0.05	8-12
1.0	8	1.13	0-4
		0.09	4-8
		< 0.05	8-12
	15	0.62	0-4
		0.05	4-8
		< 0.05	8-12
	31	0.30	0-4
		0.05	4-8
		< 0.05	8-12
	81	0.24	0-4
		0.08	4-8
		0.05	8-12
2.0	8	2.00	0-4
		0.13	4-8
		0.10	8-12
	15	1.40	0-4
		0.06	4-8
		< 0.05	8-12
	31	0.41	0-4
		0.09	4-8
		0.05	8-12
	81	0.47	0-4
		0.10	4-8
		0.07	8-12

2) The remaining data showed general residue decline but sampling at frequent enough intervals was not done to establish patterns of decline or determine half-lives.

Conclusions

1) Vinclozolin residues build up and persist longer from a series of repeat applications than from a single application.

2) A determination of the halflife and patterns of residue decline could not be established since sampling at frequent enough intervals was not done.

3) The field dissipation data was poorly presented, results that were related and should have been in one report were scattered among 4 reports. The reviewer will not organize the registrant's submission.

4) See CONCLUSIONS, part 4. below, for a synthesis and final statement on the field dissipation data.

3.17 Determination of BAS 352 F and its 3,5-Dichloraniline Containing Metabolite Residues in Soil Samples, submitted by J.A. Foushee, BASF, April 4, 1979, Report No. PR-184, acc.#098256, tab J-19.

Procedure

Three soils planted to strawberries in California, Oregon and North Dakota were treated with vinclozolin at rates of 0.25 - 2.0 lb ai/A between 4 and 12 times at 1/2 to 3 week intervals.

The respective pH and organic matter content (%) of the 3 soils were 7.2 and 1.0, 7.3 and 9.5 and 5.9 and 2.1.

Soil samples were analyzed for vinclozolin and its 3,5-dichloraniline-containing metabolites to a depth of 12 inches.

1) Residues of vinclozolin equivalents found (California test, 12 treatments)

<u>lb ai/A per treatment</u>	<u>sampling interval from last treatment (days)</u>	<u>vinclozolin equivalents (ppm)</u>	<u>soil depth (inches)</u>
0.5	179	0.18	0-4
		0.05	4-8
		< 0.05	8-12
	200	0.14	0-4
		0.07	4-8
		0.06	8-12
	353	< 0.05	0-4
		0.05	4-8
		< 0.05	8-12

(Continued)

<u>lb ai/A</u> <u>per</u> <u>treatment</u>	<u>sampling interval</u> <u>from last</u> <u>treatment (days)</u>	<u>vinclozolin</u> <u>equivalents</u> <u>ppm</u>	<u>soil</u> <u>depth</u> <u>(inches)</u>
1.0	179	0.27	0-4
		0.12	4-8
		0.07	8-12
	200	0.41	0-4
		0.11	4-8
		0.10	8-12
	353	< 0.05	0-4
		< 0.05	4-8
		< 0.05	8-12
2.0	179	0.40	0-4
		0.18	4-8
		0.17	8-12
	200	0.50	0-4
		0.22	4-8
		0.11	8-12
	353	0.15	0-4
		0.05	4-8
		0.05	8-12

2) The remaining data (Oregon and North Dakota) showed general residue decline. See conclusions in section 4. below for a discussion of all the field dissipation data.

3) Residues of vinclozolin equivalents found (North Dakota test)

<u>lb ai/A</u> <u>per</u> <u>treatment</u>	<u>number</u> <u>of</u> <u>treatment</u>	<u>sampling interval</u> <u>from last</u> <u>treatment (days)</u>	<u>vinclozolin</u> <u>equivalents</u> <u>(ppm)</u>	<u>soil</u> <u>depth</u> <u>(inches)</u>
1.0	5	227	0.90	0-6
			0.54	6-12
		336	0.25	0-6
			0.08	6-12
	4	227	1.23	0-6
			0.56	6-12
		336	0.20	0-6
			0.07	6-12
2.0	4	227	1.43	0-6
			0.79	6-12
		366	0.22	0-6
			0.11	6-12

Conclusions

1) Vinclozolin residues build up and persist longer from a series of repeat applications than from a single application.

2) Residues of vinclozolin containing the 3,5-dichloroaniline moiety can persist in soil to the next season after use of the product as recommended.

3.18 Determination of BAS 352 F and c/ts 3,5-Dichloroaniline - Containing Metabolite Residues in Soil Samples, PR-186, acc. #098256, tab J-20.

Procedure

Two soils planted to strawberries in California and North Dakota were treated with vinclozolin at rates of 0.25 - 2.0 lb ai/A between 5 and 24 times between 2 years.

The California soil had a pH of 7.2 and 1.0% OM and the North Dakota soil had a pH of 7.3 and 9.5% OM.

Soil samples were analyzed to as deep as 24 inches for parent and 3,5-dichloroaniline-containing metabolites.

Conclusions

1) Soil samples were not taken at frequent enough intervals to establish patterns of residue decline. However, the results of the analyses of soil (receiving recommended label rates of vinclozolin) at 200 days (California) after the last treatment indicate residues as high as 0.5 ppm can persist for 1 year.

2) Residues were found as deep as 24 inches in the soil. This would be expected when considered with the soil adsorption data showing low adsorption. However, this does conflict with the leaching and aged leaching data which show no leaching of parent compound and weak leaching of soil aged residues. (See sections 3.10, 3.8 and 3.9, respectively, for soil adsorption, leaching and aged leaching data).

3.19 Uptake of Aged ^{14}C -Vinclozolin (BAS F- ^{14}C) Soil Residues by Rotational Crops, Huber and Otto, Report No. 1589, September 1978, acc. #098256, tab J-21.

Procedure

Neuhofen soil (loamy sand, 83% sand, 7% silt, 10% clay, 2.6% organic carbon, pH = 6.8, CEC = 10, bulk density = 1.4) was fortified to 7 ppm with U- ^{14}C -phenyl-vinclozolin and aged aerobically in the dark at $20 \pm 2^\circ\text{C}$ for 60 or 365 days. During aging, soil moisture was kept at 40%.

Results

1) Uptake of Aged ^{14}C -Vinclozolin Residues by Rotational Crops (7 ppm soil fortification)

Treatment to planting (days)	Planting to sampling (days)	Plant part	Total ^{14}C (ppm)	MeOH extr. ^{14}C (ppm)	Intact DCA in % of total ^{14}C	Parent cpd in % of MeOH extr.	Total org. phase in % of MeOH extr.	Aqueous phase in % of MeOH extr.
60	30	soybean-aerial	3.162					
60	147	-beans	3.201					
60	147	-pods	0.851	0.350	74	4	73	28
60	147	-leaves	3.082	1.579	87	5	60	31
60	147	-roots	5.726					
365	30	soybean-aerial	0.635		66			
365	138	-beans	0.892		84			
365	138	-pods	0.508	0.165	50	10	76	32
365	138	-leaves	0.741	0.307	66	7	56	40
365	138	-roots	3.950	0.549	55	21	70	24
60	30	wheat	2.632		61			
60	98	-aerial	0.945		12			
60	98	-grain	1.818		78			
60	98	-ears	7.567	3.340	52			
60	98	-stalks	34.198		25			
365	30	wheat	1.104		37			
365	121	-aerial	0.783		7			
365	121	-grain	0.846		20			
365	121	-ears	1.079	0.649	39	12	40	61
365	121	-stalks	9.006		17			
60	30	carrot	23.533					
60	98	-tops	0.886	0.334	41	47	54	38
60	98	-roots	0.744	0.330	82	38	65	35
60	98	-leaves	1.859		54			
365	30	carrot	0.265	0.144	34	23	32	64
365	112	-tops	0.671	0.221	33	19	47	57
365	112	-roots						
365	112	-leaves						

After each aging period, summer wheat, soybeans and carrots were planted in pots containing the aged, fortified soil and grown under artificial light on a 12 hour period.

Plants were analyzed for ^{14}C content and for characterization of the ^{14}C residues using standard extraction, analytical and LSC techniques.

- 1) See chart on previous page.
- 2) Rotational crops planted in soil 2-12 months after treatment with ^{14}C -vinclozolin pick up vinclozolin residues, for example:

5-month old soybean plants contained 0.5 - 3.2 ppm residues as total ^{14}C in different aerial parts.

1-4 month old summer wheat contained 0.75 - 7.5 ppm residues as total ^{14}C in different aerial parts.

Carrots planted 2 and 12 months after treatment and harvested at 30 days growth contained 23.5 and 1.86 ppm residues in the tops as total ^{14}C , respectively; but when harvested at 3-4 months growth residue levels in the different plant parts were 0.27 - 0.89 ppm.

In most cases, greater than 1/2 of the total ^{14}C - residues contained the intact DCA moiety which was cleavable via alkaline hydrolysis. Also, between 1/3 and 2/3 of the total ^{14}C is extractable with methanol.

3) Of the samples analyzed, between 4 and 21% of the MeOH extractable residues were parent compound except for the MeOH extractable carrot residues which were 19 - 47% parent compound. The rest of the MeOH extractable activity from the soybeans contained more non-polar than polar material in the range of 1.2 - 2.5 times. The remaining MeOH extractable activity from the wheat (only 1 sample analyzed) and carrots contained more polar than non-polar material in the range of 1.3 - 7 times. The polar material consists primarily of products of molecular weight 700 - 5,000.

Conclusions

1) Crops planted in rotation to ^{14}C vinclozolin treated strawberries will pick up ^{14}C residues when planted between 2 and 12 months after treatment. (Data was not submitted showing a rotational interval when < 0.07 ppm ^{14}C residues would be picked up).

2) Total ^{14}C residues in the range of 0.51 - 5.7 ppm, 0.78 - 34.2 ppm and 0.27 - 23.5 ppm were found in different plant parts of rotational soybeans, summer wheat and carrots, respectively. The data show 1/3 - 2/3 of the total ^{14}C to be methanol extractable. See results #3 above for characterization of the methanol extractable residues.

3.20 Determination of BAS-352 F and its 3,5- Dichloroaniline -
Containing Metabolite Residues in Rotational Crop Samples, Report No.
PR-188, March 30, 1979, acc. #098256, tab J-22.

Procedure

Strawberry plots in California, Florida and North Dakota of the following respective % organic matter and pH levels, 1.0% and 7.2, 1.8% and 6.5 and 9.5% and 7.3, were treated between 4 and 12 times with cold vinclozolin at a rate of 1.0 lb ai/A. Some plots were treated at 2.0 lb ai/A four times.

Treatments were repeated at 1/2 - 3 week intervals and rotational crops were planted 2, 6 and 9 months after the last treatment.

Plants samples were hydrolyzed directly with no extraction followed by acylation of the 3,5-dichloroaniline to N-(3,5-dichlorophenyl) chloroacetamide, known as DCAD. The DCAD was quantitized and converted to vinclozolin equivalents via HPLC with a UV detector. This method is reported to average recoveries of $101 \pm 16\%$ over 0.05 - 1.0 ppm fortification levels.

Results

1) Residues of vinclozolin in rotational crops

	Rate (lb ai/A) and # applications	Planted, days after last appl.	Sampled, days after last appl.	Vinclozolin eq. found (ppm)
Carrot root	1.0, 12	183	298	0.13
Carrot top	1.0, 12	183	298	1.32
Lettuce	1.0, 12	183	268	< 0.05
Squash	1.0, 9	62	107	< 0.05
Radish top	1.0, 9	62	107	0.96
Radish root	1.0, 9	62	107	0.22
Corn grain	1.0, 9	62	129	< 0.05
Corn stalk	1.0, 9	62	129	0.38
Sugarbeet root	1.0, 5	283	435	0.06
Sugarbeet root	1.0, 4	283	435	0.05
Sugarbeet root	2.0, 4	283	435	< 0.05
Soybean	1.0, 5	283	415	0.72
Soybean	1.0, 4	283	415	0.19
Soybean	2.0, 4	283	415	0.46
Spring wheat	1.0, 5	283	412	< 0.05
Spring wheat	1.0, 4	283	412	< 0.05
Spring wheat	2.0, 4	283	412	< 0.05

Conclusions

Use of vinclozolin at recommended rates will result in residues containing the 3,5 - dichloraniline moiety in some rotational crops. See results above.

3.21 ¹⁴C-BAS 352 F Bluegill Sunfish, *Lepomis macrochirus*
Bioconcentrations Study, Prepared for BASF by Union Carbide, August 4, 1978
UCES Proj. No. 11506-80, BWC Proj. No. VIII-1-H-144, acc. # 098256, tabs
J-24 and 25.

Procedure

This is a standard flow-through bluegill sunfish bioconcentration study using phenyl-U-¹⁴C-vinclozolin. During the 30 days of uptake, the mean concentration of vinclozolin in the water was 0.465 ± 0.047 ppm, the pH was 7.7 - 8.1 and the temperature was 21.2 - 22.5 °C.

Water and fish samples were assayed for total ¹⁴C and extracted for metabolite characterization.

Results

1. Bluegill Sunfish Bioaccumulation - from tab J-24

Day	Water (ppm)	Edibles		Non-edibles		Whole fish	
		ppm	BF	ppm	BF	ppm	BF
exposure							
0	0.481						
1	0.415	19.7	47.5	82.1	197.8	60.5	145.8
3	0.492	26.6	54.1	96.6	196.3	59.6	121.1
7	0.486	34.3	70.6	136	279.8	52.1	107.2
10	0.511	48.2	94.3	143	279.8	94.8	185.5
14	0.511	50.2	98.2	154	301.4	115	225.0
22	0.387	41.1	106.2	123	317.8	93.1	240.6
30	0.435	43.9	100.9	113	259.8	91.1	209.4
depuration							
1		29.2		67.2		45	
3		16.7		28.4		22.3	
7		6.3		10.7		7.3	
10		3.7		7.6		4.5	
14		1.6		4.4		2.7	

2. The total ^{14}C values given for edible and non-edible fish tissue and for water in tab J-25 are different but not significantly.

3. Extraction and TLC Analysis of Water Samples

Day	^{14}C Extractable with ETOAc	Unextractable		Distribution of ETOAc Extract		
		^{14}C	parent	met E	met B	origin*
7	96.9	3.1	26.5	9.3	42.8	2.3
10	95.3	3.8	27.2	10.6	40.1	6.8
14	91.8	2.5	20.3	10.1	46.7	1.5
30	94.3	2.2	12.5	9.9	42.2	2.2

*Includes metabolite F

4) Extraction and TLC Analysis of Fish Tissue

Day	Fish Tissue	MeOH, ^{14}C * Extractions	Unextractable ^{14}C	Acetonitrile Partition	Hexane Partition	Distribution of Acetonitrile			
						parent	met F	unk 1	unk 2
7	edible	94.7	14.0	92.7	1.1	35.7	23.5	9.5	2.5
	non-edible	93.8	6.6	90.6	1.6	61.9	6.3	3.0	0.9
14	edible	92.1	7.4	91.4	1.2	37.3	17.5	6.0	2.3
	non-edible	92.7	6.4	90.4	1.5	51.7	7.2	2.8	0.7
30	edible	92.4	18.5	91.2	1.3	34.0	24.7	6.2	2.9
	non-edible	88.8	19.7	82.5	3.6	52.6	9.3	2.6	1.1

* The MeOH extractable ^{14}C was subsequently partitioned between acetonitrile and hexane

Conclusions

1. Bluegill will accumulate vinclozolin residues when exposed to vinclozolin contaminated water. Exposure to 0.5 ppm in the water will result in bioaccumulation levels peaking at 2-3 weeks at 100 X in the edibles, 320 X in the non-edibles and 240 X in the whole fish. These peak values will drop 97-98% after 2 weeks of depuration.

2. Accumulated residues in the fish are primarily in the form of parent compound, metabolite F and small amounts of 2 unknown compounds.

3. Since the pH of the exposure water was slightly alkaline and vinclozolin is least (hydrolytically) stable at alkaline pH's, the results showing the fish being exposed to a mixture of vinclozolin and its degradation products B and E, is expected.

3.22 ¹⁴C - BAS 352 F Channel Catfish, *Ictalurus punctatus* (Rafinesque), Bioconcentration Study, prepared by UCES for BASF, October 18, 1978, UCES Proj. NO. 11506 - 80, BWC Proj. No. VIII-1-H-144, acc. # 098256, tabs J-26 and 27.

Procedure

¹⁴C A sandy loam soil (pH=7.1) was fortified to about 9 ppm with U-phenyl ¹⁴C-vinclozolin and aged aerobically for 14 days. It was then flooded with water (pH=7.8-8.3) and aged an additional 14 days after which time the catfish were added.

Water, soil and fish tissues were analyzed for total ¹⁴C and the water was additionally extracted and analyzed for degradation products.

Results

1. Distribution of ^{14}C Activity From Catfish Uptake Study

Day	Soil	Water	Edibles		Non-edibles		Whole fish	
			ppm	BF	ppm	BF	ppm	BF
aer. soil								
aging								
0	8.97							
7	5.04							
14	5.92							
water/soil								
aging								
15	5.04	0.01						
21	6.37	0.06						
28	5.16	0.10						
exposure								
29	6.27	0.11	0.35	3.2	1.03	9.4	0.84	7.6
32	4.24	0.13	0.61	4.7	2.01	15.5	1.42	10.9
35	3.21	0.14	0.44	3.1	1.4	10.0	1.12	8.0
38	2.73	0.13	0.45	3.5	1.42	10.9	1.39	10.7
42	3.45	0.18	0.32	1.8	1.12	6.2	0.80	4.4
50	3.63	0.20	0.25	1.3	0.84	8.2	0.50	2.5
57	1.53	0.19	0.19	1.0	0.65	3.4	0.43	2.3
depuration								
58			0.05		0.13		0.10	
60			0.006		0.035		0.02	
65			0.007		0.025		0.02	
67			0.015		0.026		0.03	
71			0.012		0.029		0.03	

2. Levels of total ^{14}C in the water during exposure, as determined in the study under tab 27, were 5-10% higher than those levels recorded in the table above.

3. The major degradation product in the water at all exposure time intervals was metabolite B with small amounts of parent compound and metabolite E. The table reporting the exact amounts of these products was missing from the report. (For chemical names and structures of metabolites B and E and of the parent compound, see section 3.26, below).

Conclusions

1. Catfish will accumulate residues of soil aged vinclozolin to levels in the non-edible portion not exceeding 20 X when levels in the exposure water are 0.1 - 0.2 ppm. Accumulation levels in the whole fish and edible portions will be less.
2. Peak levels of accumulation occur at about 1 week of exposure but after 2 weeks of subsequent depuration, residues in all fish portions will drop to 2% of the peak levels.
3. Residues in the fish were not identified in this study but due to the relatively low accumulation levels and the fact that 98% of the residues are purged during depuration, residue identification will not be needed.

3.23 Determination of the Partition Coefficient of Vinclozolin in the System n-Octanol/Water, Otto, S., Lab Report No. 787, Sept, 2, 1977, acc. # 098255, tab J-3.

Procedure and method of analysis

Phenyl-¹⁴C-vinclozolin was used with standard LSC techniques.

Results

<u>ug of ¹⁴C- vinclozolin</u>	<u>ug in octanol</u>	<u>ug in water</u>	<u>Partition Coefficient</u>
48.3	47.12	0.057	826.7
487.4	474.05	0.385	1231.3
2491.0	2452.40	2.100	1167.8

Conclusions

The octanol/water partition coefficient for vinclozolin is on the order of 1,000 at 22 ± 2° C.

3.24 Determination of Partition Coefficient of Vinclozolin Metabolite B in the System Water/Octanol, Redeker, J., Lab Communication No. 830, Nov. 28, 1978, acc. no. 098255, tab J-4.

Procedure

Vinclozolin metabolite B, which is 3,5-dichlorophenyl carbamic acid (1-carboxy-1-methyl-2-propenyl ester, was partitioned between octanol and water buffered at pH 7. The buffer was used to prevent recyclization to vinclozolin.

Method of analysis

The concentration in the water phase was determined by monitoring the extinction of the maximum in recording UV spectrophotometer. Concentration in the octanol phase was determined by subtraction.

Results

<u>Octanol phase</u> <u>mg/ml</u>	<u>Water phase</u> <u>mg/ml</u>	<u>Partition Coefficient</u>
0.069	0.031	2.22
0.429	0.071	6.04
0.901	0.091	9.99

Conclusions

The partition coefficient of metabolite B of vinclozolin in the concentration range of 0.05 - 0.5 mg/ml water (pH 7) at 22° C is 2.2 - 10.0.

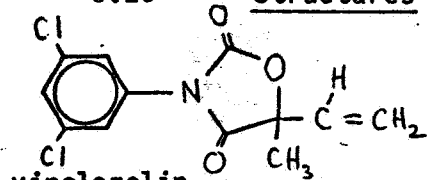
3.25 Determination of the Water Solubility of Vinclozolin,
Redeker, J., Lab Communication No. 827, November 1978, acc # 098255, tab J-5.

Conclusions

At pH=3.5, vinclozolin has the following water solubility.

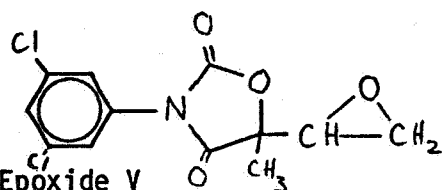
Temperature (°C)	15	25	35
Solubility (ug/ml)	8.8	13.6	15.5

3.26

StructuresWhere occursparent compound

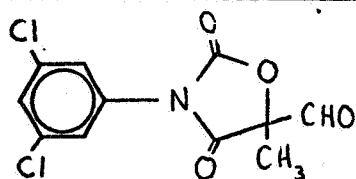
vinclozolin

3-(3,5-dichlorophenyl)-5-ethynyl-5-methyl-1,3-oxazolidine-2,4-dione



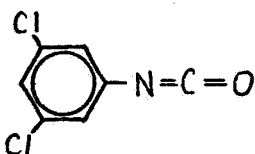
Epoxide V

3-(3,5-dichlorophenyl)-5-oxiranyl-5-methyl-1,3-oxazolidine-2,4-dione

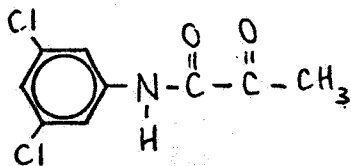
sensitized aqueous photolysis
(minor)

formyl derivative U

3-(3,5-dichlorophenyl)-5-formyl-5-methyl-1,3-oxazolidine-2,4-dione

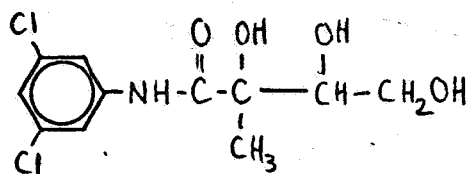
sensitized aqueous photolysis
(major)

3,5-dichlorophenyl isocyanate

sensitized aqueous photolysis
(minor)

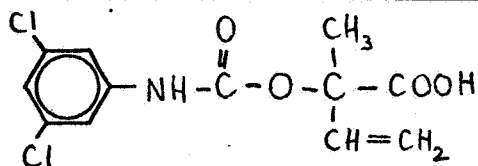
3,5-dichloropyruvic acid anilide

sensitized aqueous photolysis
(minor)



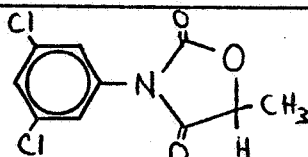
rotational soybean leaves
exposure water from fish
study
fish

metabolite F
N-(3,5-dichlorophenyl)-2,3,4-trihydroxy butanoic acid amide



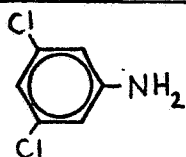
hydrolysis pH 6,9 (major)
pH 3 (minor)
soil-aerobic, anaerobic, sterile

metabolite B
3,5-dichlorophenylcarbamic acid (1-carboxy-1-methyl) allyl ester or
3,5-dichlorophenylcarbamic acid (1-carboxy-1-methyl)-2-propenyl ester



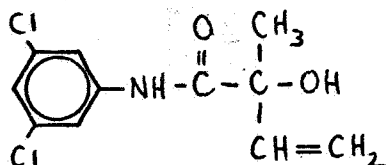
soil - aerobic

metabolite S
3-(3,5-dichlorophenyl)-5-methyl-1,3-oxazolidine-2,4-dione



soil-aerobic, anaerobic, sterile

metabolite D
3,5-dichloroaniline



hydrolysis pH 3, 6, 9
soil-aerobic, anaerobic, sterile

metabolite E
N-(3,5-dichlorophenyl)-2-hydroxy-2-methyl-3-butenic acid amide

4. CONCLUSIONS

4.1 Environmental fate profile

Vinclozolin hydrolyzes most rapidly at alkaline pH's; respective halflives at pH's 3, 6 and 9 and 25°C are 12 minutes, 61 hours and 70 days. Metabolite E is the major product formed at pH 3 but, at pH's 6 and 9 both metabolites B and E form, with 2-5 times more B forming than E. (See section 3.26 above for structures and chemical names). Vinclozolin will photolyze on soil with a halflife of 19 days forming metabolites E, S and W but will not photodegrade in water except in the presence of photosensitizers. Under photosensitization and in water, it will have a halflife of 4 hours with formyl derivative U being the major product and 3,5-dichloroisocyanate, 3,5-dichloropyruvic acid anilide and epoxide V being minor products. Epoxide V is the probable precursor to formyl derivative U.

Under aerobic soil conditions, vinclozolin will degrade at different rates depending on soil pH and soil microbe populations. Since vinclozolin degrades due to both chemical and microbial action, the contributions of the the different degradation pathways could not be determined exactly, but soil microbes do contribute more to soil degradation than does chemical action. Under alkaline (pH=7.4) soil conditions, the halflife will be 3-4 days and under slightly acid (pH=6.8) conditions, the halflife will be 3-7 weeks. This range would be expected in light of the hydrolytic fate described above. It is also noted that strawberries grow best in slightly acid (pH 5.5-6.5) soil (see Small Fruit Culture, 5th edition, James S. Shoemaker) implying relatively long halflives are to be expected. Four metabolites, B, D, E and S form under aerobic soil conditions. Metabolites B, E and S peak at 2-4 weeks and metabolite D peaks at 3 months but all 4 metabolites subsequently degrade. Degradation of vinclozolin also occurs under anaerobic and sterile soil conditions but at much slower rates than under aerobic conditions. The anaerobic soil halflife is not reached in 6 months and the sterile soil halflife is even greater. (Note that sterilization of soil via autoclaving generally lowers soil pH, which in the case of vinclozolin would increase its stability). Although some soil microbes degrade vinclozolin and some use it as a carbon source, it totally inhibits the growth of the soil blue algae Nostoc muscorum, a nitrogen fixer. Data on other nitrogen fixing organisms was not submitted and in light of the effect on N. muscorum, this data will be needed in addition to other outstanding "effects on

microbes" data as listed in the recommendations. If the data to be submitted shows N. muscorum or additional soil microbe inhibition, then deferral to EEB will be made with regard to environmental effects resulting from the soil microbe inhibition.

Soil leaching data shows the parent compound not to leach and shows only weak leaching of soil aged vinclozolin residues. This is supported by deep core soil samples taken under field use conditions showing no detectable (<0.05 ppm) 3,5-dichloroaniline-containing residues reaching 3 feet deep. Studies on field dissipation of vinclozolin after repeated applications in one season, show residues would build up from year to year when applied at the higher label rates and will especially persist in some North Dakota areas (perhaps due to the cold winters).

Rotational crops will pick up residues of vinclozolin even when less than the maximum seasonal rate has been applied. The only crops which showed no detectable residues of vinclozolin were: lettuce planted 6 months after treatment at 12 lb ai/A, squash and corn grain planted 2 months after treatment at 9 lb ai/A and spring wheat planted 9 months after treatment at 8 lb ai/A. However, for the above cases, the maximum seasonal rate of 17.5 lb ai/A was not applied. The registrant has not submitted data showing intervals with non-detectable residues in other rotational crops.

Fish accumulation data for bluegill and catfish exposed to similar water concentrations of vinclozolin show maximum bioaccumulation factors of 3/8 X and 16 X, respectively, in the non-edible parts. Residues peak in the bluegill at 3 weeks and in the catfish at 3 days and reach the highest levels in the non-edible parts. Residue levels drop, however, to 2-3% of the peak levels in all fish parts after 2 weeks of depuration. Although the catfish were exposed to soil aged residues of vinclozolin and the bluegill were tested in a flow through system receiving parent vinclozolin, analysis of both catfish and bluegill exposure water showed not parent compound but metabolite B to be predominate with smaller amounts of parent compound and metabolite E. This would be expected in light of the pH 6 and 9 hydrolysis and the aerobic soil data. Also, if vinclozolin would get into natural waters supporting aquatic life, hydrolysis to predominantly metabolite B would be expected since the desirable pH range for fresh water aquatic life is 6.5 - 9. (See Quality Criteria for Water, EPA, July 1976, page 178. Natural waters near mining areas may have a lower pH). It is noted in this case that octanol/water partitioning data on parent vinclozolin does not give a realistic indication of the propensity of

agriculturally applied vinclozolin to bioaccumulate, since it is not vinclozolin, but a mixture of it and its degradation products (mostly metabolite B) that would be exposed to non-target organisms. This point is demonstrated by the reported octanol/water partition coefficients for vinclozolin ($P=1,000$) and metabolite B ($P=6$). Alone, neither one represents the accumulation that would occur due to agriculturally applied vinclozolin.

5. RECOMMENDATIONS

5.1 We do not concur with registration of vinclozolin on strawberries.

5.2 The environmental fate of vinclozolin is not completely understood. The following data are needed:

5.2.1 Complete experimental data substantiating the statement in the sensitized photolysis study (Report No. 1599) that vinclozolin does not photolyze in water (in the absence of photosensitizers) are needed. Also, a description of the light source, wavelength range and intensity of radiation used in the photolysis studies and a profile of the soil used in the soil surface photolysis study are needed.

5.2.2 With regard to the soil metabolism studies run on European soils (Report Nos. 1571 and 1592), data are needed showing the ratios of soil bacteria to fungi to actinomycetes in the European soils and the ratios of soil bacteria to fungi to actinomycetes in American soils common to the strawberry growing areas.

5.2.3 With regard to vinclozolin effects on microbes and in light of the inhibition of Nostoc muscorum, effects on nitrogen fixation using Azotobacter and Clostridium are needed. In addition, effects on nitrification and tests measuring enzyme activity for dehydrogenase or phosphatase are needed. Also, effects on the degradation of cellulose, starch, pectin and protein must be determined using at least one each of soil bacteria, actinomycetes and molds. See the proposed guidelines in the Federal Register (July 10, 1978, vol. 43, No. 132, page 29718, section 163.62-8(f)(3)).

5.3 The rotational crop data permits rotation only to the following and only when the indicated total pounds active ingredient applied per acre has not been exceeded through the previous season.

5.3.1 Lettuce may be planted 6 months after treatment not exceeding 12 lb ai/A.

5.3.2 Squash may be planted 2 months after treatment not exceeding 9 lb ai/A.

5.3.3 Corn may be planted 2 months after treatment not exceeding 9 lb ai/A with use of only the corn grain for food and/or feed purposes.

5.3.4 Spring wheat may be planted 9 months after treatment not exceeding 8 lb ai/A.

5.4 Other uses of vinclozolin may require additional data on environmental fate.

5.5 Note to PM - For rotational crop restrictions to be used in regard to the EUP submission 7969-EUP-RG, see section 5.3 and its subsections 5.3.1 - 5.3.4, above.

Samuel M. Creeger
February 20, 1980
Review Section # 1
Environmental Fate Branch
Hazard Evaluation Division

Samuel M. Creeger
March 4, 1980