

Influence of Continuous Monoculture and Insecticide Treatments on the Rate of Chlorfenvinphos Soil Biodegradation in Cabbage Crops

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Chlorfenvinphos [diethyl 1-(2,4-dichlorophenyl)-2-chlorovinyl phosphate] is one of the most used soil insecticides in Europe for cabbage crop protection against root fly. It is very efficient, and nothing has been reported about accidental lack of efficiency when it is used in cauliflower crops.

During assays of 1986, we observed that in the soil of cauliflower crops, chlorfenvinphos $(\underline{1})$ was metabolized into 2,4-dichlorophenacyl chloride $(\underline{2})$, 2,4-dichloroacetophenone $(\underline{3})$, ∞ -(chloromethyl)-2,4-dichlorobenzyl alcohol $(\underline{4})$, 1-(2',4'-dichlorophenyl)-ethan-1-ol $(\underline{5})$, 2,4-dichlorobenzoic acid $(\underline{6})$, 2-hydroxy-4-chlorobenzoic acid $(\underline{7})$, and 2,4-dihydroxybenzoic acid $(\underline{8})$ (Rouchaud et al., 1988). In the present work, we report the results of the soil biodegradation studies of chlorfenvinphos in cauliflower crops made in 1987. Moreover, we extended that study to Brussels sprouts and chinese cabbage crops. We tried to correlate the differences as to the rates of soil biodegradation in both 1986 and 1987 assays with climate and agricultural factors, and with adaptation of the soil microbial population to insecticide soil treatments.

MATERIALS AND METHODS

Cauliflower (cv. Alpha-Balanza) were planted in different fields (65x50 cm interplant distance) at the 4-6 leaf stage at St Kate-lijne-Waver (Research Station for Vegetables), Opdorp, Oppuurs, and Gembloux (School for Horticulture). Brussels sprouts (cv. Titurel) were planted (4-6 leaf stage; 65x50 cm) at Staden (Provincial Research Station for Agriculture and Horticulture, Rumbeke). Chinese cabbage (cv. Hong Kong) were planted (4-6 leaf stage; 50x30 cm) at St Katelijne-Waver (Research Station for Vegetables) and at Gembloux (School for Horticulture). In each field, there were four replicates. Just after cabbage planting, chlorfenvin-phos was applied onto the soil by pouring around the stem of the plant an emulsion of Birlane WP (25 g% chlorfenvinphos) in water. The dose was always 50 mg of chlorfenvinphos plant-1. For sampling, soil was taken in a 10 cm radius around the stem of the plant. No residue was found at lower depth. The flower of cauli-

flower, the Brussels sprouts itself, and the whole chinese cabbage were sampled for analysis at the normal harvest.

The analytical procedures for analysis of chlorfenvinphos and its metabolites have been described (Rouchaud et al., 1987). For standards, chlorfenvinphos was prepared from Birlane WP; the standards of the metabolites were purchased from Janssen, Belgium.

For analysis of compounds $\underline{1}$ to $\underline{5}$, soil was extracted successively with acetone and acetone+water, and with heating to reflux. Acetone was evaporated, the aqueous solution was extracted with methylene chloride, the concentrated methylene chloride solution was cleaned by one or two thin-layer chromatographies (t.l.c.), and the bands were analyzed as such by gas liquid chromatography (g.l.c.) and mass spectrometry (m.s.) (Rouchaud et al., 1987).

The soil, already extracted by acetone+water, was further extracted with NaOH 1 N in water (heating to reflux) for extraction of compounds $\underline{6}$, $\underline{7}$ and $\underline{8}$. The water solution was made acid, extracted with methylene chloride, the concentrated methylene chloride solution was cleaned by one or two successive t.l.c., the bands were treated with diazomethane, and analyzed by g.l.c. and m.s. Plants were analyzed in the same way as soil (Rouchaud et al., 1987).

RESULTS AND DISCUSSION

Chlorfenvinphos ($\underline{1}$) gave excellent protection for all the cauliflower, Brussels sprouts and chinese cabbage crops against root fly. When soil biodegradation of chlorfenvinphos was enhanced by previous long monoculture and continuous insecticide soil treatments, chlorfenvinphos soil concentrations at harvest were low and protection against root fly was always good (Van de Steene, 1988). This indicated that the specific insecticide activity (insecticide activity/g of chlorfenvinphos) of chlorfenvinphos against root fly is very high. No residues of chlorfenvinphos or of its metabolites were detected at harvest in the flower of cauliflower, in the Brussels sprouts itself, and in the whole chinese cabbage; the concentrations of these compounds thus being lower than the analytical limit of sensitivity, i.e. 0.02 mg kg⁻¹ fresh weight.

Only the organophosphorus molecule of chlorfenvinphos $(\underline{1})$ has an insecticide activity. Chlorfenvinphos metabolites are not insecticidal; their measurement in soil give an evaluation of the kinetics of the complete metabolism of chlorfenvinphos in soil.

The histories of the crop fields of cauliflower, Brussels sprouts or chinese cabbage were different as to the number of years (since 1986) of preceding continuous monoculture and insecticide treatments (Table 1). The same fields were used in 1986 and 1987. Chinese cabbage crops were grown on fields next to the ones of

TABLE 1. 1	Field hist	TABLE 1. Field history, soil analysis, and duration and rainfall for the assays	nalysis,	and durati	on and rai	nfall for	the assays		1
Field his	Field his Soil analysis	lysis				Assays of 1986	1986	Assays of 1987	1987
tory,	핊	Sand, %	Lime, %	Clay, %	Organic	Duration	Rainfall	Duration Rainfall	Rainfall
yearsa					matter,%	of the	during	a)	during
						crop, days g	crop,	crop, days 8	crop, mm h
1. Crops	1. Crops of cauliflower:	ower:							
1.1. Spri	ng crops:								
St Kateli	St Katelijne-Waver, SKW:	SKW:							
2 b ,e	5.6	72.3	22.3	5.4	3.3	43	132	57	158
Opdorp:									
9 9	5.9	75.1	14.9	10.0	2.8	22	126	65	160
Oppuurs:									
$18\overline{b}$	5.7	59.9	29.8	10.3	3.5	20	126	65	160
1.2. Summer crops:	er crops:								
SKW:									
2 b ,e	as in 1.1. SKW	1. SKW				57	59	51	172
Opdorp:									
q 9	as in 1.	as in 1.1. Opdorp				57	59	63	119
Oppuurs:									
18b	as in 1.	as in 1.1. Oppuurs				57	59	63	119
Gembloux,	School fo	School for Horticulture:	ure:						
1b	5.5	10.2	74.8	15.0	2.4			52	207
2. Brusse	ls sprouts	2. Brussels sprouts crops at Staden:	taden:						
2c	5.5	60.2	29.4	10.4	2.5	138	206	112	404
3. Chines	3. Chinese cabbage crops:	crops:							
SKW									
2d	as in 1.1. SKW	1. SKW						45	100
Gembloux,	School fo	Gembloux, School for Horticulture:	:nre:					•	
1d	as in 1.	as in 1.2. Gembloux						42	94

TABLE 2. Biodegradation of chlorfenvinphos in the soil of cauliflower, Brussels sprouts and chinese cabba-

biodegradation of chlorienvinphos in the soil of cauliflower, brussels sprouts and chinese cabba- made in 1987.	(mg of equivalents of	8 Total			nd 22.1				nd 26.3						2.5 21.3							0.8 9.5			nd 19.3		
russels sprou	abolites	7	b:	nd	2.2	3.5	2.9		pu	1.9	3.4	3.1		pu	4.2	0.4	3.9					3.4			2.9		
rlower, b	d of its r	6 6 6 6 6 6 6 6 6 6 6 6 6 6 6 6 6 6 6	Spring (pu	1.8	2.3	2.3		pu	1.7	2.5	2.0		pu	3.7	4.5	2.8		pu	5.5	4.3	1.7		pu	6.8	3.5	1.9
or cauli	inphos an	5 01 4 16	KW: 1.1.1	pu	0.05	0.1	0.2		pu	0.02	0.03	0.05		pu	0.1	0.2	0.05		pu	pu	0.1	pu		pu	0.2	0.1	0.1
TIME SOIT	chlorfenv	4 mean	Waver, S	pu	0.1	0.5	0.2		pu	0.1	0.1	0.2		nd	pu	0.3	0.2		pu	pu	pu	0.2		pu	0.3	0.3	9. 0
ıı souduı	soil of	3 411 %	Katelijne	pu	0.4	0.3	0.3		pu	0.2	0.4	0.1		pu	0.05	0.02	0.05		pu	0.05	0.1	0.05			0.1		
chlorien	centrations in soil of chlorfenvinphos and	1 2 3 4 5 6	.1. At St	pu	2.4	3,3	3.1		pu	2.5	3.2	2.3	ing crop:	pu	8.9 1.9 0.	3.4	2.5		pu	2.3	2.7	1.6	ring crops	pu	7 2.3	3,5	2.8
adation or 1987.	i	1	iflower: 1	25.3	15.1	7.6	6.2		26.3	15.3	8.1	3,9	1.2.1. Spr	23.4	8.9	3.6	1.8	:dc	24.1	8.5	7. 0	1.8	1.3.1. Sp	22.8	6.7	3.1	1.4
. blodegra s made in	Delay,	uays	of caul	0	13	34	22	Summer crop	0	11	29	51	Opdorp:]	0	21	42	65	Summer cro	0	18	07	63	Oppuurs:	0	21	42	65
IABLE 2.	Date		1. Crops	22-4	55	26-5	18-6b	1.1.2.	20-7	31-7	18-8	9 - 6	1.2. At	14-4	5-5	26-5	18-6b	1.2.2.	31-7	18-8	6-6	2-10b	1.3. At	14-4	5-5	26-5	18-6b

Concentrations in soil of chlorfenvinphos and of its metabolites (mg of equivalents of chlorfenvinphos kg-1 dry soil; means of 4 replicates)	8 Total					1.2 9.5					0.5 13.2												nd 23.3		0.5 16.7	
metabolites (m	7																						pu			
d of its plicates)	9		pu	6.9	7.4	2.6		pu	3.6	3,3	2.4		pu	3.1	3.2	1.8	0.7		pu	1.3	1.4		pu	1.5	3.4	
inphos and of 4 reg	2	 	pu	0.2	0.3	0.3		pu	0.05	0.2	0.2		pu	pq	pu	pu	pu		pu	0.1	0.2		pq	0.1	0.2	
chlorfenv	7		pu	0.3	0.2	0.2		pu	0.2	0.4	0.4		pu	0.1	0.1	pu	nd		pu	0.2	0.4		pu	0.1	0.2	
centrations in soil of chlor orfenvinphos kg ⁻¹ dry soil;	3		pu	0.1	0.2	pu		pu	0.05	0.1	pu		pu	0.2	0.1	0.1	pu	SKW:	nd	0.3	0.3		pu	0.2	0.1	
ations in vinphos k	2		pu	1.9	2.7	1.3		pu	1.4	2.3	2.1		pu	1.6	2.5	1.1	0.3	: 3.1. At	nd	1.9	2.4		pu	2.1	3.1	
Concentr chlorfer	1		23.9	7.5	1.9	1.0		23.6	11.2	6.3	4.5	s crop at	23.9	8.6	3,3	1.9	8.0	se cabbage	25.1	13.9	7.5		23.3	13.1	5.6	
Delay, days		Summer crop	0	18	07	63	Sembloux:	0	21	39	52	els sprouts	.,	26	62	85	112	of chinese	0	22	45	Sloux:	0	24	42	
Date Delay, Con days chl		1.3.2. S	31-7	18-8	6-6	2-10b	1.4. At (19–6	10-7	28-7	10-8b	2. Brusse	27-5	22-6	28-7	20–8	16-9p	3. Crops	18-8	6-6	2-10b	3.2. Gem	10-8 0	36	21 - 9b	

Dates are the ones of sampling, day-month, year 1987; superscript b indicates the harvest date. nd=not detected.

TABLE 3. Half-lifes in soil and concentrations in soil of chlor-fenvinphos and of the sum of chlorfenvinphos+all its identified metabolites at harvest (mg of equivalents of chlorfenvinphos kg⁻¹ dry soil; in the half sphere of 10 cm radius around the stem of the cabbage plant. Dose of treatment: 50 mg chlorfenvin-phos/plant

pnos/plant.				
	Chlorfenvinp	hos	Chlorfenvin	phos+metaboli-
			tes	
	t1/2, days	mg kg-1	t1/2	mg kg-1
1. Crops of	1986: 1.1. Sp	ring crops of	cauliflower:	
SKW	23	4.3	50	13.0
Opdorp	10	2.9	50	12.5
Oppuurs	9	0.4	50	10.0
1.2. Summer	crops of caul	iflower:		
SKW	30	7.9	70	16.9
Opdorp	20	7.0	70	17.0
Oppuurs	16	7.6	80	17.0
Gembloux	17	2.9	50	9.0
1.3. Brussel	s sprouts cro	p at Staden:		
	22	1.6	65	3 . 7
2. Crops of	1987: 2.1. Sp	ring crops of	cauliflower:	
SKW	20	6.2	70	15.2
Opdorp	12	1.8	70	12.8
Oppuurs	9	1.4	62	12.0
2.2. Summer	crops of caul	iflower:		
SKW	17	3.9	55	12.8
Opdorp	10	1.8	53	9.5
Oppuurs	9	1.0	52	9.5
Gembloux	18	4.5	60	13.2
2.3. Brussel	s sprouts cro	p at Staden:		
	20	0.8	60	3 . 4
2.4. Chinese	cabbage crop	s:		
SKW	24	7 . 5	60	15.0
Gembloux	22	5.6	65	16.7

cauliflower, and which had the same field histories and soil analyses. In previous years, several organophosphorus insecticides (diazinon, trichloronate...) other than chlorfenvinphos had been used. Table 1 gives crop duration, i.e. the number of days from planting until harvest, and cumulative rainfall during crop.

Table 2 reports soil biodegradation of chlorfenvinphos $(\underline{1})$ in crops made in 1987. Formula of compounds $\underline{1}$, $\underline{2}$, $\underline{3}$... are given in the introduction.

The rate of chlorfenvinphos $(\underline{1})$ soil biodegradation in cauliflower crop was always faster at Oppurs than at Opdorp, and especially than at St Katelijne-Waver. The rate ratio for chlorfenvinphos soil biodegradation (that is the ratio of the rates of chlorfenvinphos soil biodegradation in fields of different locals and histories as to previously continuous monoculture and insecticide treatments) could be as high as 2.6 (Table 3). This was observed during both 1986 and 1987, and during both spring and summer

crops. Summer of 1986 was an exception; it was very dry, and soil microbial activity was low; this induced a levelling effect, the rate ratio for chlorfenvinphos soil biodegradation being reduced to 1.9. For the sum of chlorfenvinphos+all its metabolites, the rate ratios were always approximately 1.0. Similar results were observed with cauliflower crops at Gembloux, Brussels sprouts crops at Staden, and chinese cabbage crops at both St Katelijne-Wayer and Gembloux.

In St Katelijne-Waver, Opdorp and Oppuurs, soil analyses were similar. These locations are only 20 km apart in the same plain.

In 1984 and 1985, crops of cauliflower had been done on another field at St Katelijne-Waver (soil SKW 1984-5). That field was very next to the one of the assays of 1986 and 1987 (soil SKW 1986-7). Both fields had the same soil analysis, and had been fertilized in the same way. However, on the field of the assays of 1984+1985 (soil SKW 1984-5), cauliflower crops had been made continuously since 7 years with insecticide soil treatments. In laboratory experiments, chlorfenvinphos was incorporated into the soil SKW 1984-5 and in the one from the field at Oppuurs onto which were made the assays of 1986+1987 (soil Oppuurs 1986+87); after 2 months of incubation at 20°C in the laboratory, the rates of disappearance of chlorfenvinphos were similar in both soils. When the same experiment was done with the soil of SKW 1986+7 and with the soil Oppuurs 1986+7, biodegradation of chlorfenvinphos was 5 times faster in the soil of Oppuurs 86-7 than in the soil SKW 86-7 (De Smet and Dejonckheere, 1988).

These results indicate that the main cause of the differences in rates of chlorfenvinphos soil biodegradation, in crop fields of different locals, are mainly due to the different field histories, i.e. the number of years of preceeding monoculture and continuous soil insecticide treatments.

When, in separate experiments, chlorfenvinphos was incorporated into sterilized soil and incubated for more than 2 months at 20°C in the laboratory, we observed that the rate of disappearance of chlorfenvinphos in soil was more than fifteen times lower than that observed in unsterilized field soil. Biodegradation of chlorfenvinphos in unsterilized field soil thus mainly occurred by microbial processes. The results observed in the field thus indicate that a long history of continuous cauliflower monoculture, with soil insecticide treatments, generated adapted microbial populations and higher rates of chlorfenvinphos biodegradation.

In laboratory experiments, Suett (1986) observed that carbofuran soil disappearance was faster when the soil had been treated repeatedly with carbofuran in previous years. Soil biodegradation enhancement of pesticide by repeated soil treatments made with the same product, has also been observed for pesticides other than carbofuran (Walker and Suett, 1986). Felsot et al. (1982) obtained similar results.

With the assays reported here, during the preceding years, soil treatments against root fly had been done with soil insecticides (trichloronate, diazinon...) other than chlorfenvinphos. Adaptation of soil microbial populations to insecticides different from chlorfenvinphos thus induced highest rates of chlorfenvinphos soil biodegradation. Soil microbial population adaptation to one insecticide thus could be generated by previous continuous soil treatments with other insecticide molecules, and by continuous monoculture.

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