

Fate of the Insecticide Chlorfenvinphos in the Soil of Cauliflower Field Crops

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Control of root flies in cabbage crops has always been and remains difficult (Pelerents 1982). Chlorfenvinphos (diethyl 1-(2,4-dichlorophenyl)-2-chlorovinyl phosphate) is an insecticide used widely and efficiently against root flies in cabbage culture. Several metabolites of chlorfenvinphos ($\underline{1}$) in soil have been identified: 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 ($\underline{5}$) (Beynon et al. 1966, 1967 and 1968). Their soil concentrations are always very low; they are very transient intermediates and represent only a small part of chlorfenvinphos metabolites.

In the present work, we searched for the metabolites of chlor-fenvinphos which are found in higher concentrations in soil of cauliflower crops. These metabolites make up a part of the soil bound residue of chlorfenvinphos.

MATERIALS AND METHODS

Cauliflower were planted in the field at the 4-6 leaf stage. Just after planting, 50 mg of chlorfenvinphos was applied onto the soil by pouring around the stem of the plant an emulsion of Birlane WP (25 g% chlorfenvinphos) in water. Crops were made in four different locations in Belgium which were different as to their soil types. At St Katelijne-Waver: pH 5.6, sand 72.3%, silt 22.3%, clay 5.4%, organic matter 3.3%, loamy sand. At Opdor: pH 5.9, sand 75.1%, silt 14.9%, clay 10.0%, organic matter 2.8%, sandy loam. At Oppuurs: pH 5.7, sand 59.9%, silt 29.8%, clay 10.3%, organic matter 3.5%, sandy loam. At Gembloux: pH 5.5, sand 10.2%, silt 74.8%, clay 15.0%, organic matter 2.4%, silt loam. In each field there were four replicates. Soil was sampled around the cauliflower stem, taking a volume of soil corresponding to half a sphere having a radius of 8 cm. No residue was detected at lower soil depth.

In order to evaluate the loss of chlorfenvinphos by evaporation from soil, the insecticide was incorporated separately in sterilized sand from the Rhine, and in sterilized soil from Opdorp at +Send reprint resquests to J. Rouchaud at address 1.

the 50 ppm level using Birlane WP. Sand and soil were previously wetted so that they contained 25% g/g water. Incubation was at 20°C in an open beaker. Chlorfenvinphos in sand and soil was measured 15, 30 and 45 days after soil incorporation.

Standard chlorfenvinphos $(\underline{1})$ was prepared from Birlane WP. Birlane WP (100 g) was mixed with chloroform (300 ml), the mixture was filtered, the solution was concentrated (vacuum evaporator at 30°C) during which chlorfenvinphos crystallized. Recrystallization afforded a product > 97% pure. From Janssen Belgium were obtained the metabolites $\underline{2-5}$, and of 2,4-dichlorobenzoic acid $(\underline{6})$, 2-hydroxy-4-chlorobenzoic acid $(\underline{7})$, and 2,4-dihydroxybenzoic acid $(\underline{8})$.

Thin layer chromatography (t.1.c.) was performed using silicagel plates (Merck). The analyzed solution was applied as a band. The standards were applied on a part of the t.1.c. plate.

Chlorfenvinphos and its metabolites 2-5 were analyzed as such by gas liquid chromatography (g.l.c.). Metabolites 6, 7 and 8 were methylated with diazomethane before g.l.c. analysis. Chlorfenvinphos was detected using a flame photometric detector. Compounds 2-8 were detected by electron capture. Injection and detection at 250°C, glass column 1.80 mx2mm i.d. filled with 5% SE30 on 80-100 mesh Gas Chrom Q, nitrogen carrier gas at 80 ml/min. Metabolite, oven temperature, retention time: 1, 200°C, 4.2 min; 2, 150°C, 2.3 min; 3, 125°C, 3.6 min; 4, 160°C, 3.5 min; 5, 160°C, 1.8 min; 6 (methylated), 140°C, 2.2 min; 7 (methylated) 140°C, 3.3 min; 8 (methylated), 140°C, 4.5 min.

Several times, compounds $\underline{1}$, $\underline{2}$, $\underline{6}$, $\underline{7}$ and $\underline{8}$ were analyzed by mass spectrometry (m.s.). When separated on t.1.c., they were scraped, extracted with ethyl acetate, this was concentrated and analyzed by m.s. (without methylation of acids 6-8).

Soil (100 g) was extracted with acetone (200 ml) with stirring and heating to reflux during 2 hr; after cooling and filtration, the solid residue was extracted in the same way with acetone+ water 1+1 (200 ml). The extracts were gathered, concentrated to 130 ml. After addition of NaCl, the mixture was extracted two times with methylene chloride (2x200 ml). This was dried with sodium sulphate, concentrated and applied on a first t.l.c. plate. Elution with ethyl acetate gave a band at Rf=1.0 containing the compounds 1-5. The band was separated, extracted with ethyl acetate, concentrated, and applied on a second t.l.c. plate. Elution with chloroform gave (metabolite, Rf): 2 and 3, 1.0; 4, 0.72; 5, 0.45; 1, 0.25. A band containing metabolites 2+3 was isolated; an other large one was isolated which contained metabolites 1+4+5. The silicagel was extracted, concentrated, and analyzed by 1.c. and m.s.

The acetone and acetone+water extracted soil was extracted with NaOH 1 N in water (200 ml) with stirring and heating to reflux

during 1 hr. After centrifugation, the supernatant was made acid (HCl), the mixture was extracted with ethyl acetate; this was dried (Na $_2$ SO $_4$), concentrated and applied on a t.l.c. plate. Elution with 2-propanol+33% ammonia+water 7+1.5+3 v/v/v separated the acid metabolites (metabolite, Rf): 6: 0.82; 7, 0.68; 8, 0.32. The bands were separated, extracted with ethyl acetate, methylated with diazomethane when they were analyzed by g.l.c. but not when they were analyzed by m.s., concentrated and analyzed by g.l.c. and occasionally by m.s. The recoveries in soil of chlor-fenvinphos and of its metabolites were 65-105%. The flower of cauliflower was extracted in the same way as soil, but the first extraction was made using a Sorvall omnimixer.

RESULTS AND DISCUSSION

In all four crop locations, no root fly attack was observed, good protection being obtained with chlorfenvinphos. No chlorfenvinphos nor any of its metabolites were detected in the flower of cauliflower, the analytical limit of sensitivity for these compounds being about 0.02 mg kg fresh weight. Fourty five days after incorporation of cauliflower into sterilized sand or soil, more than 95% of the applied dose was measured as chlorfenvinphos itself in sand and soil. Losses of chlorfenvinphos by evaporation from soil thus are very low.

Results (Table 1) indicate that, beside chlorfenvinphos (1) 2,4-dichlorophenacyl chloride (2) is the main acetone soluble metabolite of chlorfenvinphos in soil. It is generated by hydrolysis of chlorfenvinphos. The ∞ -(chloromethy1)-2,4-dichlorobenzyl alcohol (4), which is generated by reduction of the ketone function of 2, is present only in low concentrations in soil. The reduction which consisted into the replacement of the aliphatic chlorine atom by a hydrogen one also did not occur intensively, as shown by the low soil concentrations of 2,4-dichloroacetophenone (3) and of 1-(2',4'-dichloropheny1)-ethan-1-o1 (5). These results are different from the ones obtained during soil incubation of chlorfenvinphos in laboratory conditions (Beynon et al. 1967); indeed, during these last assays, soil concentrations of $\frac{2}{2}$ were very low, whereas concentrations of the reduction metabolites 3 and 5 were rather high.

In the acetone and acetone+water insoluble residue, thus in the soil bound residue, we identified 2,4-dichlorobenzoic acid (6), 2-hydroxy-4-chlorobenzoic acid (7) and 2,4-dihydroxybenzoic acid (8). Compound 6 should be generated successively by hydrolysis of 2,4-dichlorophenacyl chloride, oxidation into 2,4-dichlorophenylglyoxylic acid (which could not be detected in any of the soil extracts), and decarboxylation into 6. Compounds 7 and 8 correspond to the progressive replacement into 6 of chlorine atoms by hydroxyl groups. When looking for loss of chlorfenvinphos by evaporation from sterilized soil or sand, 45 days after incorporation of the insecticide in sand or soil, more than 95% of the chlorfenvinphos was still present as such in sand or soil.

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	20		126	0. 4	2.5	0.05	7.0	0.1	1.0	3,3	1.2	9.95

TABLE 1	TABLE 1, Continuation.										
Dated	Days at	1	Chlorten	vinphos a	Chlortenvinphos and metabolites (as equivalents of chlorienvinphos) soil con-	lites (as	equivaled	ots of chi	Lorienvir	tos (soud	_r con_
	בֿב		רבוורו מרז	OIIS, IIIB.R	B uty S	אדר (יוובמוזכ	7 7 7	ידדרם רבים ל			-
	treat-	rain-	- 1	7	m]	41	∽ I	<u> </u>	<u>-1</u>	∞I	Total
	IIICIII C	IIII									
3. Crop	at Oppurs	3									
3.2. Sun	.2. Summer crop										
14-7	0	0	24.9	pu	pu	pu	pu	pu	pu	pu	24.90
1-8	18	11	11.5	1.5	0.05	0.2	0.1	7.9	1.7	pu	22.95
19-8	36	19	10.2	1.8	0.1	0.2	0.2	6.3	1.5	0.7	21.00
9 - 6	57	59	7.6	1.6	0.05	0.4	0.3	2.7	3.1	1.2	16.95
4. Crop	. Crop at Gembloux	nx									
9-9	0	0	24.5	pu	pu	pu	pu	pu	pu	pu	24.50
4-7	28	62	5,3	1.5	0.05	0.2	0.05	5,3	3,5	pu	15,95
25-7	67	95	6.4	1.7	0.05	0.4	0.1	2.2	3,3	0.3	12.95
1-8	56	96	3.5	1.8	0.05	0.4	0.2	1.5	2.0	0.5	9.95
12-8b	29	121	2.9	1.9	pu	0.5	0.1	1,1	2.2	0.3	00.6
a. Samol	ing date.	dav-mont	h. vear 1	.986							
b. Cauli	flower ha	rvest.		· !							
c. nd=nc &-(ch1c	n detecte romethyl)	d. 1: chl -2,4-dich	orfenvinp lorobenzy	hos; 2: 2 1 alcohol	c. nd=non detected. 1: chlorfenvinphos; 2: 2,4-dichlorophenacyl chloride; 3: 2,4-dichloroacetophenone; 4: \(\omega - \text{(chloromethyl)} - 2, \overline{4} -	rophenacyl',4'-dichl	chlorid loropheny	e; 3: 2,4- [)-ethan-]	-dichlorc L-ol; <u>6</u> :	acetopher 2,4-dich]	oroben-
מסור מכי	n. 7 • 7 • n.	yuroxy-4-	CIITOI ODEII	מזרי מנזח	7.0	ı tııyuı oayı	שוובטור מי	• T.			

Compounds $\underline{6}$, $\underline{7}$ and $\underline{8}$ thus should arise in field soils through microbial mechanisms. Their concentrations in soil were rather high; thus, on account of their relative stability, they tend to accumulate in soil.

For the spring crops made in St Katelijne-Waver, Opdorp and Oppuurs, the rate of chlorfenvinphos disappearance (also of the sum chlorfenvinphos+metabolites 2-8) was in the following decreasing order: Oppuurs Opdorp St Katelijne-Waver. This could be related to soil composition, especially the clay content.

For the summer crops made in St Katelijne-Waver, Opdorp and Oppuurs, the rate of chlorfenvinphos disappearance, and the rate of disappearance of the total chlorfenvinphos+metabolites <u>2-8</u> were similar in the three locations. Moreover, these rates of disappearance were lower than during the spring crops, in spite of the higher temperatures. This could be related to the unusual dry weather during the summer crops, soil dryness having a levelling effect on the rate of insecticide metabolism.

The soil at Gembloux contains more clay and silt than soils in the other crop regions. In spite of that, the rate of disappearance of chlorfenvinphos and of the total chlorfenvinphos+metabolites $\underline{2}$ to $\underline{8}$ were not high. Moreover, good protection against root fly was obtained with chlorfenvinphos at Gembloux.

Results obtained in the four different regions show the influence of soil texture, rainfall and season on the rate of chlorfenvin-phos metabolism in soil. Identification and measurement of the major metabolites of the bound residue give a better measurement of the total fate of chlorfenvinphos in field crops. The results give information about the true chlorfenvinphos concentrations in soil during cauliflower growth, and thus about the protection against root fly.

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REFERENCES

- Beynon, K.I., Davies, L., Elgar, K., Stoydin, G. (1966). Analysis of crops and soils for residues of diethyl 1-(2,4-dichlorophenyl)-2-chlorovinylphosphate. J. Sci. Fd Agric. 17, 162-174.
- Beynon, K.I., Wright, A.N. (1967). The breakdown of ¹⁴C-chlorfenvinphos in soils and in crops grown in the soils. J. Sci. Fd Agric. 18, 143-150.
- Beynon, K.I., Edwards, M.J., Elgar, K., Wright, A.N. (1968).
 Analysis of crops and soils for residues of chlorfenvinphos insecticide and its breakdown products. J. Sci. Fd Agric. 19, 302-307.

Pelerents, C. (1982). Basisgegevens voor een beredeneerde bestrij

ding van de koolvlieg, Delia Brassicae Bouche. IWONL Centrum voor de geintegreerde bestrijding van insekten. Rijksuniversiteit Gent, Gent, Belgium.

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