THE BREAKDOWN OF LAMBDA-CYHALOTHRIN IN COTTON GROWING SOIL

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Abstract

The breakdown of lambda-cyhalothrin in cotton growing soil was studied in an indoor incubation experiment. Lambda-cyhalothrin was incubated at 30˚C in the dark in soil with different water contents. The degradation rate was similar at three water contents ranging from 30% to 90%. Degradation in shaken aqueous soil slurry was faster than in unsaturated soil, possibly due to the better redistribution of the lambda-cyhalothrin. The study indicated that degradation of this compound followed first-order kinetics and the half-life of this compound in different soil water contents was calculated to be in the range of 19-37 days. Degradation was apparently biological, as it was prevented by heat sterilisation and sodium azide. The isomerization of lambda-cyhalothrin also occurred in this experiment.

Introduction

Lambda-cyhalothrin [α-cyano-3-phenoxybenzyl-3-(2-chloro-3,3,3 -trifluoropro-1-enyl)-2,2-dimethyl cyclopropanecarboxylate] is a broad spectrum synthetic pyrethroid insecticide. It has become one of the most widely used pyrethroids, since the 1986-1987 season, in cotton production systems in Australia for use in Stage II of the widely accepted pyrethroid strategy (Forrester, 1989). Because pyrethroids, including lambda-cyhalothrin, are very toxic to fish and crustaceans (Hill, 1989), there is concern about their possible persistence in the environment. The present studies were undertaken to determine the rate of dissipation of this compound in cotton growing soil in controlled conditions.

Materials and Methods

The grey-cracking soil was collected from a cotton field in Narrabri in New South Wales. Air dried soil (pH 8) was placed in 250 mL glass bottle, a solution of lambda-cyhalothrin in acetone (100 μg/mL) was added to 1 g of the soil and the solvent allowed to evaporate, well mixed with 9 g of soil before adjusting the water content to 30%, 60%, 90%, 200%, and 400%. The soil was well mixed, the jar capped and incubated in the dark at 30˚C. The saturated soil samples (200% and 400% water content) were shaken orbitally at 160 rpm at 30˚C. The sterile soil experiment was carried out at the same time as control. The sterile soil samples were adjusted to 60% water content. The final concentration of lambda-cyhalothrin was 10 ppm (mg/kg).

The residue analysis method was adapted from those previously reported for fenvalerate and deltamethrin in soils (Hill, 1981, 1983). At interval of 0, 2, 4, 6, and 8 weeks, soil samples were analyzed in whole without subsampling. To the soil samples with 2 mL water/g and 4 mL water/g, 5 mL freshly shaken slurry were removed from each jars for analysis. The samples, contained in 250 mL capped jars, were equilibrated with 4 mL of 0.1 N acetic acid for 1 h and then were extracted on a Certomat Braun rotary platform shaker at 160 rpm according to the following regime: 17 mL of acetone for 1.5 h, 13 mL of 1:1 v/v hexane-acetone for 1.5 h, 13 mL of 1:1 v/v hexane-acetone for 15 min, followed by a 5-min

rinse with 17 mL of hexane. Between solvent changes, the soil was allowed to settle and the liquid extract decanted through prewashed glass wool to 250 mL separatory funnel using pasteur pipettes. Combined extracts were liquid-liquid partitioned with 60 mL of 2% NaCl, the hexane layer was separated, and the aqueous layer was re-extracted with a fresh 17 mL of hexane. Combined hexane extracts were dried by passage through anhydrous Na_2SO_4 into a 250 mL glass-stoppered round bottom flask. The solvent extract was then rotary evaporated (<40˚C) to a small volume, and transferred quantitatively to a 10 mL volumetric flask and adjusted to 10 mL with hexane in a volumetric flask.

Extracts were cleaned up on acid alumina Pasteur pipette columns (7 mm i.d). Acid alumina (2.8 g at 6% moisture) was added and packed down by tapping the column. Anhydrous sodium sulphate was added so that the height above the alumina was about 1 cm. One mL of extract was applied. The extract was washed in with 2 mL of hexane and this 2 mL wash was discarded. The lambda-cyhalothrin was eluted with 10 mL of 1:6.7 v/v ether-hexane and the eluate was collected in a 50 ml pear shaped flask for evaporation of the ether to about 1 mL in a rotary evaporator. This was quantitatively transferred to a 10 mL volumetric flask in which the volume was made to 10 mL with hexane. Samples were stored in a deep freeze (minus 20˚C) until analyses were performed. Depending on the concentration of lambda-cyhalothrin residues, the eluate was either diluted or applied directly to the gas chromatograph.

Lambda-cyhalothrin extracts were analyzed on a DB-5 capillary column in a Shimadzu GC8A gas chromatograph with ECD. The details of the gas chromatographic conditions are shown in Table 1. Confirmation of the identity of the peaks was obtained using a Hewlett Packard 5890 Series II gas chromatograph interfaced with a 5971 mass selective detector allowing determination of mass spectra.

Results

Isomeric forms of lambda-cyhalothrin

Two peaks were visible on the chromatograms for standards of lambda-cyhalothrin with injection amounts greater than 180 pg, using the DB-5 column. One was relatively small, together with a larger peak eluting immediately afterwards. These are concluded to be isomeric forms of lambda-cyhalothrin. Mass spectrometric analysis showed that these two peaks have identical mass spectra. In this paper, these peaks are named as isomer 1 for the small peak, and isomer 2 for the large peak.

Isomerization of lambda-cyhalothrin in soil

The concentration of isomer 1 of lambda-cyhalothrin with different water content for five sampling dates are shown in Figure 2. This data shows that the isomerization of lambda-cyhalothrin occurred in soil when incubated at 30˚C in the dark. There are previous reports of isomerization of this compound in the sunlight (Curl *et al*., 1984; French and Leahey, 1990), but no reports of isomerization in soil under dark conditions. A alkaline soil pH value (8.0) may be responsible for this phenomenon because another experiment showed that the isomerization is accelerated in sterile buffers as pH is raised above 7.

The data also shows that soil water content can affect the net level of the isomer 1 in soil. With the same soil water content, the rate of conversion of two isomers in sterile soil was faster than in the non sterile treatment. El Beit *et al.* (1981) have indicated that sodium azide may increase the pH of soil when it is added to soil as a sterilant. This may have influenced the rate of conversion of two isomers under these conditions in the current study.

Biodegradation of lambda-cyhalothrin in soil

The effect of soil sterilization on the dissipation of lambda-cyhalothrin is shown in Figure 2. Losses (total isomers) from sterile and nonsterile soils at 30˚C were compared over a period of 8 weeks. The levels of lambda-cyhalothrin in the hexane-acetone extracts decreased in both the sterile and nonsterile treatments. However, the decrease in the nonsterile treatment was much faster, only 31% remaining after 8 weeks at 30˚C, indicating that heat labile agents such as microorganisms are much more important than purely chemical factors in the disappearance of lambda-cyhalothrin. This result clearly suggests that dissipation of lambda-cyhalothrin in soil, like other kinds of pyrethroids, is mostly microbial. The loss of lambda-cyhalothrin (total isomers) under the sterile condition (after 8 weeks, 83% remained) is most likely due to chemical hydrolysis because this compound is known to be susceptible to alkaline

conditions (Collis and Leahey, 1984). Experiments have shown that the dissipation of this compound (total isomers) occurs in sterile buffers with pH values greater than 7. However, at pH 7 in sterile buffer, the concentration of this compound (total isomers) did not decline during 4 weeks incubation. Volatilisation from the soil surface would not be expected to contribute much to the dissipation of this compound because of its low vapour pressure, although this was not tested. Flasks were sealed, so this factor was not assessed.

Mathematical modelling of lambda-cyhalothrin degradation in incubated soil

The dissipation of lambda-cyhalothrin in soil with different water content at 30˚C is shown in Figure 3. The data are plotted as the concentration remaining (both isomers) in the soil on a logarithmic scale against of incubation in weeks and the straight lines shown are those of best fit calculated by regression analysis (Fig. 3). The straight line relationships obtained indicate that dissipation of lambda-cyhalothrin in the incubated soil followed first-order kinetics.

The effect of soil water content on dissipation

Linear regression analysis produces a set of equations shown in Table 2. The half-lives calculated from the slopes of the lines together with the correlation coefficient for the lines of best fit are shown in Table 3.

The half-lives at the same initial pyrethroid concentration and the same temperature were different for different soil water contents. The greater the water content, the shorter the half-life. This effect was more apparent with shaken soil suspensions. This effect can also be seen from the different dissipation rate of this compound from soil.

The analysis shows that the slopes of the three regression are not significantly different between 30% and 90% water content, indicating that the rate of dissipation of lambda-cyhalothrin was similar at these three water contents. The slopes of the regression in these water contents do not differ significantly, however, and can be averaged to give a value of 0.063 with a standard deviation of 8.1%. The corresponding half-life for lambda-cyhalothrin is 35 days in unsaturated soil. Between 200% and 400% water content, the degradation rate was not significantly different and the average slope was 0.134, with the half-life in slurried soil calculated to be shorter at 21 days.

Thus, the lambda-cyhalothrin in shaken soil slurry degraded more rapidly than in unsaturated soil, by a factor of about 1.7. The reasons for this may be due to (1) better redistribution of lambda-cyhalothrin in the soil suspension decreasing the sorption of this compound to the soil and then made more amounts available for degradation. (2) better condition in the soil suspension stimulated microbial activity.

Discussion

Lambda-cyhalothrin was shown to degrade rapidly from the cotton farming soil and the dissipation of this compound in the incubated soil under laboratory conditions followed first-order kinetics. The dissipation of lambda-cyhalothrin was accelerated in the non-sterile treatments, indicating that microorganisms contributed a significant proportion of the observed losses of this compound. This is in agreement with the conclusions of other research workers that the dissipation of pyrethroids is mostly microbial (Kaufman *et al.*, 1977; Williams and Brown, 1979; Chapman *et al.*, 1981).

The greater the water content of the soil, the shorter half-life, and this effect was more apparent with shaken soil suspensions. The biodegradation rate observed in these studies

suggests that, under field conditions, there is no accumulation of lambda-cyhalothrin in cotton-growing soil from one season to the next. Although 10 ppm is a relatively high level of insecticide in soil, similarly high concentrations are likely at the soil surface where spray is deposited.

The non-biological losses observed in the sterile treatment containing lambda-cyhalothrin are likely to be due to chemical hydrolysis. This explanation is proposed because this compound is susceptible to alkaline hydrolysis (Collis and Leahey, 1984) and has low

volatility.

From the results presented in this paper, it is concluded that isomerization of lambda-cyhalothrin can also occur in soil under dark conditions, although there is no other documentation of this phenomenon.

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Table 1. Gas chromatographic conditions.

Column Brand:	ECONO-CAP DB-5 (5% phenyl / 95% methyl) capillary
Dimensions:	30 m x 0.54 mm (i.d) x 1.2 μm film thickness
Flow rate:	4 mL/min
Make-up gas:	26 mL/min
Column:	240˚C
Injector/Detector:	270˚C

Table 2. Regression equations of degradation rates.

Water content	Equation
0%:	Log_{10} [Residue (total isomers)] = 1.004 - 0.0570 t
0%:	Log_{10} [Residue (total isomers)] = 1.016 - 0.0640 t
0%:	Log_{10} [Residue (total isomers)] = 1.030 - 0.0675 t
200%:	Log_{10} [Residue (total isomers)] = 1.124 - 0.1285 t
400%:	Log_{10} [Residue (total isomers)] = 1.080 - 0.1390 t

where t= time (weeks) from lambda-cyhalothrin application.

Table 3. Half-lives of lambda-cyhalothrin (total isomers) in the incubated soil under laboratory conditions.

Water content	Half-life (days)	Correlation coefficient
30 %	37.0	0.994
60 %	32.9	0.981
90 %	31.2	0.977
200%	16.4	0.932
400%	15.1	0.975

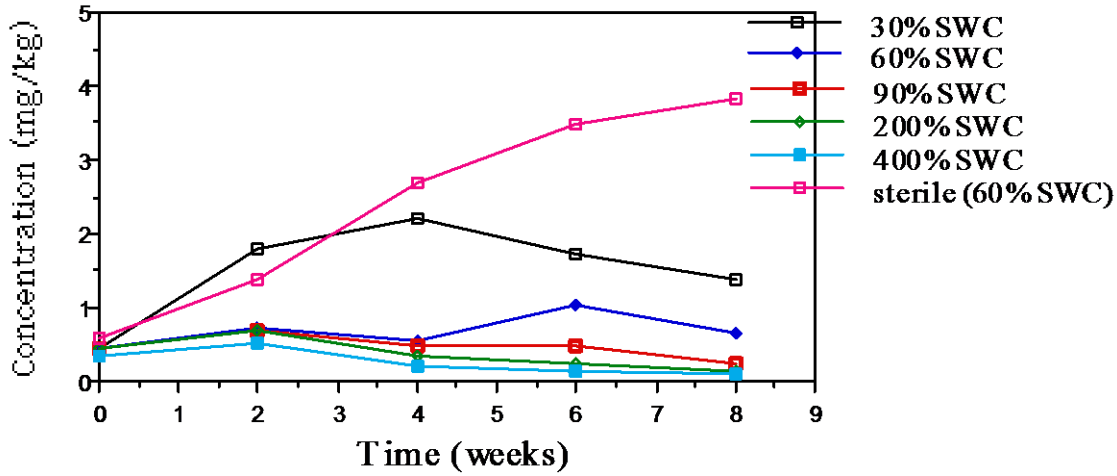

Figure 1. Change of concentration of isomer-1 of lambda-cyhalothrin in the incubated soil with different water content (SWC) under laboratory conditions.

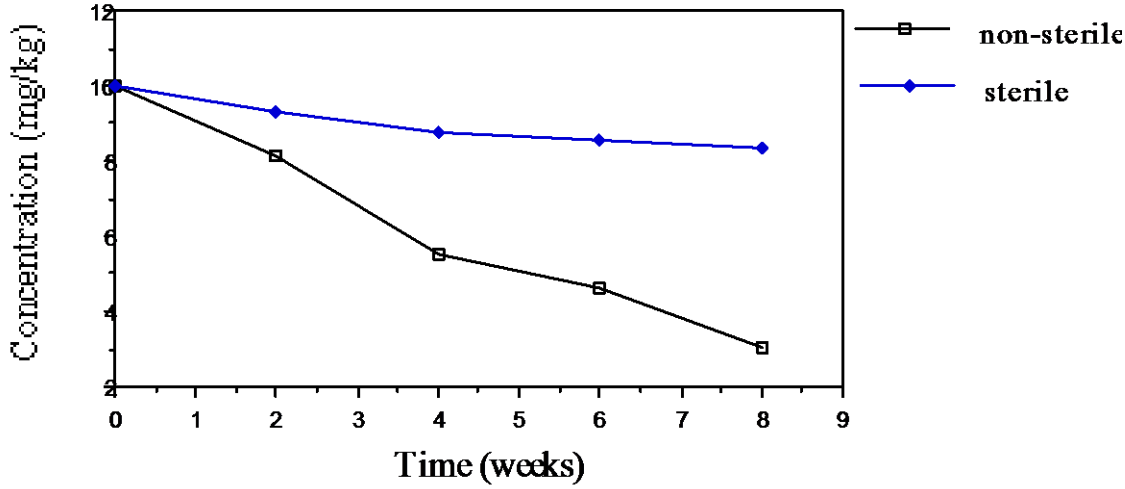

Figure 2. Dissipation of lambda-cyhalothrin (total isomers) from the incubated soil with 60% water content under laboratory conditions.

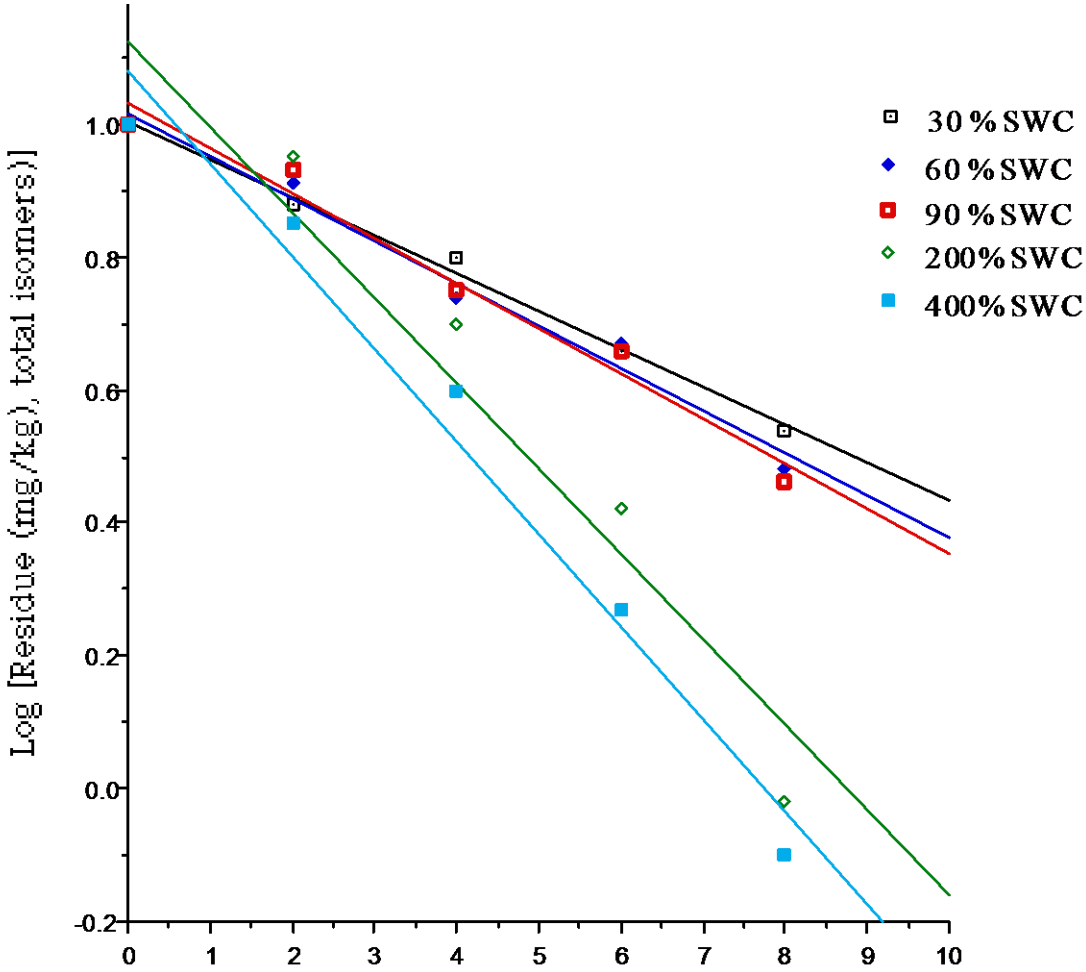

Figure 3. Relationship between log [lambda-cyhalothrin residue (total isomers)] in the incubated soil and time under laboratory conditions.