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Persistence of Five Pyrethroid Insecticides in Sterile and Natural, Mineral and Organic Soil

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A knowledge of the relative importance of chemical and biological processes in the transformation of pesticides in the environment is useful in understanding their behaviour and using them to maximum advantage. Biological degradation has been confirmed for a number of organochlorine (OC), organophosphorus (OP), and carbamate insecticides (TU & MILES 1976, WILLIAMS 1977). Many of the OP's and carbamates are degraded more rapidly than the OC's and this fact has made it possible to separate the chemical and biological contributions to degradation by examining their persistence in natural and sterile media for a few wks. In soil, biological degradation has been found to predominate for at least 12 OPs (GETZIN 1968, GETZIN & ROSEFIELD 1968, LICHTENSTEIN et al. 1968, MILES et al. 1979) and 2 carbamates (TUCKER & PACK 1972, GETZIN 1973). The pyrethroid insecticides, permethrin, cypermethrin, decamethrin, fenpropanate and fenvalerate are theoretically susceptible to both chemical (hydrolysis, oxidation) and biological degradation. They are relatively non-persistent in soil (KAUFMAN et al. 1977, ROBERTS & STANDEN 1977a, 1977b, WILLIAMS & BROWN 1979, HARRIS et al.in press, CHAPMAN & HARRIS, in press) therefore lending themselves to similar study. KAUFMAN et al. (1977) observed a reduced rate of CO_2 evolution and higher recovery of permethrin in sodium azide sterilized soil. WILLIAMS and BROWN (1979) found that both permethrin and fenvalerate disappeared more slowly in two soils after autoclaving. Both results suggest that biological processes are important for degradation in the soil. We wish to describe our results on the relative importance of chemical and biological processes in the degradation of 5 pyrethroids applied to soil.

MATERIALS AND METHODS

The soils used and the methods of sterilization, insecticide treatment, incubation and microbial population determination were as described previously (MILES et al. 1979) except that the experiment was terminated at 16 wk when all sterilized soils were determined to be microbially active (>2500 colonies/g). Insecticide treatments were theoretically 1 ppm based on oven dry soil. Parathion and DDT treatments were included to provide a link with previous experiments and as a test for the maintenance of aerobic conditions. To extract the insecticide from the 50 g (dry wt) of soil remaining after sampling for microbial population and pH determinations, it was quantitatively transferred

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to a 450-mL bottle with 100 mL of acetone, the bottle was sealed with an aluminum foil lined cap and tumbled end-over-end at ca. 30 rpm for 1 h. The acetone extract was separated from the soil by suction filtration using a Buchner funnel and Whatman No. 1 paper. The soil residue in the funnel was rinsed with a further 25 mL of acetone and the total filtrate, ca. 125 mL, was quantitatively transferred to a 500-mL separatory funnel. For DDT and the pyrethroids, the acetone extract was diluted with 250 mL of water and extracted twice with 50 mL of hexane. The combined hexane extracts were stored over sodium sulfate in a freezer until analyzed. Parathion was extracted by adding 100 mL of chloroform to the acetone extract and washing the resulting mixture 3 times with 250 mL of water. The resulting chloroform extract was treated with sodium sulfate and freezer-stored until analyzed.

Extracts of DDT and pyrethroid treated mineral soils were analyzed by GLC without cleanup (CHAPMAN & SIMMONS 1979) with the column at 200°C for DDT. Corresponding extracts of organic soils were solvent exchanged to hexane to remove traces of acetone and were cleaned up (CHAPMAN & HARRIS 1978) before GLC analysis. DDT was eluted from the deactivated Florisil used with 100 mL of hexane. Stereoisomer analysis was done as described by CHAPMAN & HARRIS (1979). Extracts of parathion treated soils were solvent exchanged to hexane and analyzed by GLC without cleanup using the instrumentation and parameters described previously for chlorpyrifos (SEARS & CHAPMAN 1979).

RESULTS AND DISCUSSION

It had previously been shown that 0.5 and 5 ppm of these pyrethroids in a mineral soil had no long term effects on the microbial populations measured over 4 wk (TU 1980). The primary purpose of the population counts in this experiment was as a sterility test. However, as observed previously under these experimental conditions (MILES et al. 1979), microbial populations in both types of natural soils declined over the 16 wk period, e.g. for bacteria from 107 X 10^5 to 8 x 10^5 colonies/g and from 30 X 10^5 to 11 X 10^5 colonies/g and for fungi from 12 x 10^3 to 1.2 x 10^3 colonies/g and from 8 x 10^3 to 1.6 x 10^3 colonies/g in mineral and organic soil respectively. Bacterial and fungal populations were <300 and <50 colonies/g respectively in all sterilized samples for at least 4 wk. Some samples of mineral soil had bacterial contamination (>2500 colonies/g) at 6 wk but fungal contamination was not observed until 8 wk. The number of contaminated samples increased with time and at 16 wk all were considered contaminated (>2500 colonies/g) with both bacteria and fungi. The contamination of these samples is reflected in the increased variability in the concentrations of the pyrethroids observed.

Maximum soil pH ranges observed over the course of the experiment were as follows: natural mineral 8.0-8.1; sterilized mineral 7.7-8.1; natural organic 7.1-7.2; sterilized

organic 6.5-6.9. Differences of this size between natural and sterilized samples were not considered large enough to have an effect on the rate of chemical hydrolyses that might take place when compared with the known effect of pH changes on the hydrolysis rates of these materials in homogeneous aqueous solution.

The rate of degradation of parathion in this experiment was identical to that observed previously (MILES et al. 1979) for both the mineral and organic soil thereby permitting the current data to be compared directly with their earlier results on the OP materials. The concentration of DDD (0.02 ppm) in the DDT treated soil did not change during the experiment even in the organic soil at 60% of its moisture holding capacity. As DDT is rapidly converted to DDD under anaerobic conditions, this clearly shows that the experimental conditions were aerobic.

All of the insecticides degraded more slowly in the sterilized soils than in the natural soils (see Fig. 1 and Table 1) indicating that heat labile agents such as microorganisms are much more important than purely physical or chemical processes in the disappearance of these materials. The return of microbial

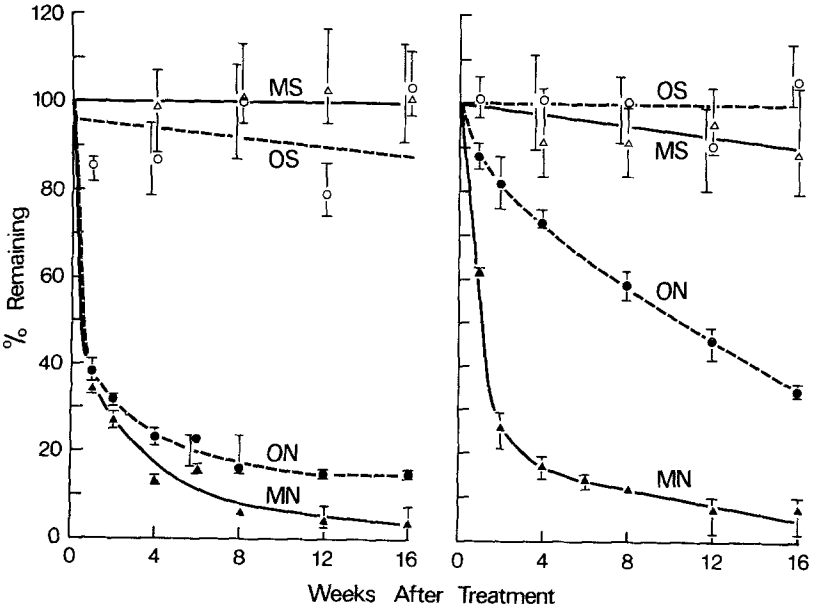

Figure 1. Persistence of permethrin (left) and fenvalerate (right) in natural (N) and sterilized (S), mineral (M) and organic (O) soils.

TABLE 1

Persistence of pyrethroid insecticides in sterilized and natural soils

	Per cent of initial application (1 ppm) remaining 8 wk after treatment			
	Mineral		Organic	
Insecticide	Sterilized	Natural	Sterilized	Natural
Parathion	80	< 2	95	6
Fenpropanate	94	2	83	8
Permethrin	101	6	100	16
Cypermethrin	93	4	92	16
Fenvalerate	91	12	100	58
Decamethrin	97	52	106	74
DDT	92	89	100	76

activity to the sterilize samples between 6 and 16 wk did not consistently lead to a rapid degradation of the pyrethroids. This observation is consistent with those made in the earlier study of OP insecticides in the same soils. Sub-critical levels or inhomogeneous distribution of contamination, lower activity of contaminating species, or the presence of more readily available energy sources in the sterilized soil are possible explanations.

The effect of both the structure and stereochemistry of the pyrethroids on the rate of hydrolysis and the rate and stereospecificity of oxidation by various microsomal systems (SODERLUND & CASIDA 1977a, b, CASIDA & SODERLUND 1977, SHONO et al. 1979), mammals (ELLIOTT et al. 1976, GAUGHAN et al. 1977a, b, HUNT & GILBERT 1977, GAUGHAN et al. 1978, RUZO et al. 1978) and insects (SHONO et al. 1978) has been described. In general hydrolysis rates were dependent on the configuration of the side chain at cyclopropane C-3 in the acid moiety while rates of oxidation were not. Variations in the substituents on this side chain influenced the rate of oxidation of all isomers but only the rate of hydrolyses of the trans isomers. Substitution of a cyano group at the α-carbon of the m-phenoxybenzyl alcohol moiety reduced both the rate of oxidation and hydrolysis. These rates were also dependent on the configuration of the carboxyl bearing carbon for both the cyclopropanecarboxylic acid and the substituted acetic acid components.

In the current study cis:trans, 1S,cis:1R,cis, and 1S,trans:1R,trans ratios were determined for permethrin and cypermethrin in an effort to provide further information on the degradation occurring in soil. The cis:trans ratio for residual permethrin in both the mineral and organic soil (see Table 2) did not change continuously or to the extent that was observed in earlier experiments (HARRIS et al. in press, CHAPMAN & HARRIS in press), where

TABLE 2

Ratios of GLC responses for permethrin and cypermethrin isomers remaining in natural soil

Soil		Permethrin			Cypermethrin		
Type	Time (wk)	cis/ trans	1S,cis/ 1R,cis	1S,trans/ 1R,trans	cis/ trans	1S,cis/ 1R,cis	1S,trans/ 1R,trans
Mineral	0	0.45	1.5	1.4	0.77	1.5	1.1
	1	0.63	1.4	1.3	1.11	2.1	0.82
	2	0.56	NA[1]	NA	1.43	1.9	0.90
	4	0.56	NA	NA	0.91	ND[2]	ND
	6	0.53	NA	NA	0.71	ND	ND
	8	0.53	1.5	1.2	0.71	ND	ND
Organic	0	0.38	1.5	1.4	0.71	1.5	1.1
	1	0.59	1.8	1.2	1.11	1.8	0.92
	4	0.59	NA	NA	1.43	1.7	0.67
	8	0.59	1.6	1.3	1.67	1.7	0.67
	16	NA	NA	NA	2.00	1.7	1.0

1. Not analyzed.
2. Not determinable because of low level.

the ratio changed from 0.67 to 2.0 within 8 wks. KAUFMAN et al. (1977) also have reported an unexplained difference between the behaviour of the cis and trans isomers of permethrin in soil and in aqueous suspensions of microorganisms from various sources. The 1S,cis:1R,cis and 1S,trans:1R,trans ratios (see Table 2) also did not vary greatly over 8 wks in contrast to our earlier studies where preferential metabolism of the 1S,trans isomer was observed. In the case of cypermethrin the cis:trans ratio did show greater and more regular changes particularly in the organic soil where the trans isomers disappeared more quickly. There appeared to be a slight preference for the degradation of the 1S,trans isomer in the organic soil and for the 1R,cis and 1S,trans isomers in the mineral soil but these observations only span 2 wk before the residues were reduced to levels which made this analysis unreliable. If the specificity of the oxidase and esterase activities observed with the microsomal systems of mammals and insects were present in the microorganisms and/or other degrading agents in the soil one would conclude that degradation observed in this experiment was taking place by both hydrolytic and oxidative processes. If one or the other process were to predominate one would expect a greater change in the cis:trans and/or 1R,trans:1S,trans ratios of permethrin and cypermethrin than was observed.

Table 1 clearly shows there is a considerable range in the susceptibility of the materials to degradation in soil. Decamethrin and fenvalerate were the least susceptible particularly in the organic soil. Fenvalerate and model compounds containing the acid or alcohol moiety of decamethrin were the materials most resistant to the esterase or oxidase activity in liver microsomes (SODERLUND &

CASIDA 1977a, b). Permethrin and cypermethrin were both degraded much more rapidly. In our earlier studies permethrin was less persistent than cypermethrin when incorporated into soil. The model studies would predict both of these materials to be more readily degraded than decamethrin as the acid moiety is a more readily hydrolyzable and oxidizable dichloro derivative rather than a dibromo bompound and also is a mixture containing the more readily hydrolyzed trans (in particular 1S,trans) isomers. Cypermethrin might be expected to be less susceptible to degradation than permethrin because of the α-cyano substitution in the alcohol component. Fenpropanate was degraded most rapidly in both the current and earlier experiments and this would not have been predicted from the behaviour of model compounds with liver microsomes.

In summary, heat labile factors, assumed to be microorganisms, play a major role in the degradation of pyrethroid insecticides in soil. Degradation rates in soil are, in part, dependent on structure but also on as yet undertermined variables. The results of isomer ratio measurements suggest that both oxidative and hydrolytic processes are operative.

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