Influence of Some Soil Characteristics on the Dissipation Rate of Landrin Insecticide

by

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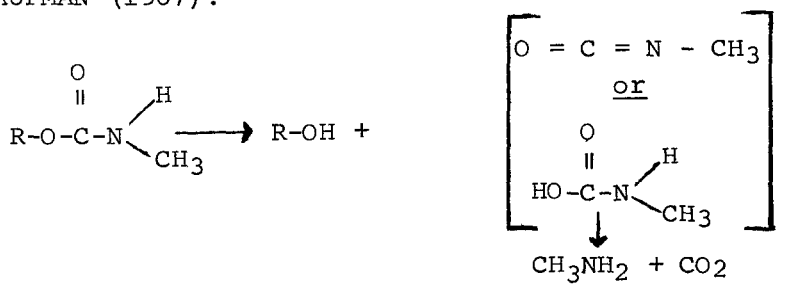
Landrin (Shell Chemical Co.; a mixture of approximately 75% 3,4,5- and 18% 2,3,5-trimethylphenyl methylcarbamate) is an effective wide-spectrum soil insecticide. The technical grade crystalline material has a vapor pressure of 5.0 x 10^{-5} mm of Hg and a water solubility of 58 ppm at 23° C; it is unstable in alkaline solution; its half-life in water is 42 hours at pH 8.0 and 38° C [Shell Tech. Bull. ACD:67-101 (1967)].

Little is known about the degradative mechanisms of methylcarbamates in soil. However, a probable degradation pathway has been suggested by KAUFMAN (1967):



SLADE and CASIDA (1970) found hydroxylated ring compounds as the major metabolites of Landrin in bean plants and houseflies; the parent compounds were metabolically short-lived.

The present report evaluates the persistence of Landrin and the influence of soil type in 8 California soils of widely divergent types.

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Experimental

Materials and apparatus. Technical grade Landrin (93% purity) and 1-fluoro-2,4-dinitrobenzene (EKC) were used without purification. Organic solvents were reagent grade or technical grade distilled in all-glass apparatus. Gas chromatographic (glc) measurements were made with an Aerograph A600B instrument with a tritium foil electron-capture detector and a 2-ft x 1/8-in. stainless steel column containing 5% DC-200 on 80/100 mesh Gas Chrom Q, with column temperature 197°C and nitrogen carrier gas flow rate 45 ml/min.

Soil treatment and extraction. Twenty-four 10-g subsamples of each air-dried soil were weighed into 2-oz screw-cap bottles and 1.0 ml of a 100 μg/ml solution of Landrin in acetone was added to each bottle. The bottles, in a hood, were rotated until acetone vapors were no longer detectable. Each subsample was then moistened with water to 67-78% of its saturation percentage, capped, and incubated at 37°C; triplicate samples were analyzed at intervals up to 24 days.

For extraction, 20 ml of acetone was added to a bottle which was then shaken mechanically for 30 min. The resulting slurry was filtered into a 250-ml separatory funnel containing 100 ml of 5% NaCl solution; bottle and filter were rinsed into the funnel with 20 ml of acetone. The filtrate mixture was partitioned into 50 ml of dichloromethane; the organic layer was washed with 100 ml of water and transferred to a 100-ml beaker.

Hydrolysis, dinitrophenylation, and gas chromatography. To the beaker was added 10 ml of 0.02 M NaOH solution and the resulting mixture was gently boiled on a hot plate until all organic solvents were expelled. This hydrolyzed mixture was transferred to a 125-ml separatory funnel and the beaker was rinsed into the funnel with 15 ml of 0.02 M NaOH solution. Three ml of 1-fluoro-2,4-dinitrobenzene solution (5% w/v in acetone) was added and the mixture was shaken 2 min. Then 25 ml of 1.0 M NaOH solution and 10.0 ml of n-hexane were added; after shaking 1 min the aqueous layer was discarded. About 5 ml of the n-hexane layer was drained into a 10-ml vial containing 1 g of anhydrous Na_2SO_4. One- to 5-μl aliquots of this solution were injected into the gas chromatograph. Responses as peak heights were compared with those from Landrin standards.

Results and Discussion

Development of analytical method. Direct application of glc is generally unsatisfactory for monomethylcarbamates because on-column decomposition usually occurs and because detector response is weak unless the carbamate contains a group (e.g., halogen or nitro) sensed by a highly specific detector. Usually, these compounds are determined via derivatives (of either the phenol or the amine moiety of the carbamate) which are amenable to glc and also detectable at the ng level. The method of COHEN et al. (1969) for trace glc determination of phenols as their 2,4-dinitrophenyl ethers was selected for this study based on simplicity of derivative formation and thermal stability of derivative produced.

Both methods described by COHEN et al. (1969) for derivative formation in solution were tried: better yields of the 2,3,5- and 3,4,5-trimethylphenol derivatives were obtained from reaction in aqueous media at room temperature than under reflux conditions in acetone. Their aqueous method was modified by substituting aqueous NaOH solutions for water-plus-saturated NaOMe as the reaction media. Within the range 0.0025 - 0.10 M NaOH solution maximum glc response was obtained with 0.02 M solutions.

The minimum time to completely hydrolyze Landrin standards in 0.02 M NaOH solution was also established. To 125-ml separatory funnels each containing 25 ml of 0.02 M NaOH solution were added 1.00-ml aliquots of 100 µg/ml Landrin in acetone; at intervals after this addition the dinitrobenzene reagent was added and the glc response of the resulting derivative was measured. Results (Table I) indicated that 100 µg of Landrin was completely hydrolyzed within 5 min.

TABLE I
Time required to hydrolyze Landrin

Hydrolysis period (min)	Peak height for 3,4,5-trimethylphenol derivative (chart divisions)			
	Replicates			Average
5	61.9	60.4	63.0	61.8
10	66.2	65.1	62.0	64.4
15	61.0	61.2	59.1	60.4
20	61.9	67.1	60.1	63.0
30	67.5	59.4	61.5	62.9

Gas chromatograms showed 2 peaks (2.9 and 3.9 min) corresponding to derivatives of the two trimethylphenol isomers. Quantitative measurements were based on

height of major peak, the 3,4,5-derivative. Although peak heights for the 3,4,5-derivative did not vary appreciably with hydrolysis time, those for the 2,3,5-derivative increased with time indicating that hydrolysis of 2,3,5-trimethylphenyl methylcarbamate was slower than for the 3,4,5-isomer.

Hexane and dichloromethane were tested as partitioning solvents: hexane gave 53% recovery compared to 92% for dichloromethane. For triplicate determinations of 10-, 20-, 30-, 40-, and 50-μg quantities of 3,4,5-trimethylphenol in soil, a relative standard deviation of 3.8% was obtained for the total method. Using 1-μl injections the minimum detectable quantity (signal-to-noise ratio of 2:1) was 0.05 ng of Landrin.

HOLDEN (1970) has reported use of this same reaction for determination of carbamates. Also, LAU and MARXMILLER (1970) have reported a residue method for Landrin by trifluoroacetylating the intact molecule.

Persistence of Landrin in soil. The persistence of Landrin in 8 moist soils at 37°C was studied. The soils and their characterizing properties are listed in Table II.

TABLE II
Some characteristics of soils used

Soil	pH	% Organic matter	Saturation percentage[a]
Meloland	7.9	0.3	28
Lahontan	7.9	1.0	33
Mohave	6.5	0.3	23
Rosamond	8.4	0.8	40
Laveen - A	8.7	0.1	21
Laveen - B	8.9	0.3	29
Mocho	7.9	1.9	45
Farallon	7.0	0.8	18

[a] Saturation percentage is determined on a saturation soil paste preparation obtained by method 2 in Agricultural Handbook No. 60, p. 84 (1954), Saline and Alkali Soils, U.S.D.A./ARS, Soil and Water Conservation Research Branch, U.S. Government Printing Office, Washington, D.C.

Following fortification with 10 ppm of Landrin the air-dried soils were moistened to 67-78% of their saturation percentages and kept in closed containers during incubation to prevent losses through volatilization. Persistence curves for Landrin in these soils are in Figure 1 A and B.

Recoveries may be slightly inflated since no attempt was made to separate unhydrolyzed Landrin from its hydrolysis products, the isomeric trimethylphenols. However, experiments with the Mocho soil indicated only a negligible error was introduced by omission of such a separation step. Thus, 10-g samples of air-dried Mocho soil were fortified with 100 µg of Landrin or with 50 µg of 3,4,5-trimethylphenol. At intervals these samples were moistened (3.0 ml of water/10 g of soil), extracted, and reacted with 1-fluoro-2,4-dinitrobenzene. Recoveries (Table III) showed no significant change in extraction efficiency for Landrin vs. contact time; however, only 13% of the 3,4,5-trimethylphenol applied was recovered after 3 days in the air-dried soil. This loss with time may be due to chemical or biological conversion of the phenol or to its strong adsorption by the soil so as to make it unavailable for extraction.

TABLE III
Replicated recoveries of 10 ppm of Landrin and 5 ppm of 3,4,5—trimethylphenol from Mocho soil

3,4,5-Trimethylphenol				Landrin			
	Recovered				Recovered		
Days	(ppm)			Days	(ppm)		
0	6.6	6.4	6.2	0	6.9	7.0	7.0
1	3.6	3.3	-	3	6.7	6.8	-
2	2.3	2.0	-	7	7.0	7.3	-
3	1.1	1.4	-	10	6.8	8.6	-
-	-	-	-	16	7.0	7.8	-

As was mentioned earlier, the hydrolysis rate was slower for 2,3,5-trimethylphenyl methylcarbamate than for the 3,4,5-isomer. This observation is confirmed when examining gas chromatograms of extracts of Landrin-treated soils from which most of the Landrin applied has disappeared. For these soils the ratio of peak heights for the 2,3,5- and the 3,4,5-trimethylphenol derivatives is much higher than for technical grade Landrin (ratio ~1:4). This ratio change would occur if the 3,4,5-trimethylphenyl methylcarbamate was hydrolyzed to a greater extent than the 2,3,5-isomer.

The effects of soil pH over the range 6.5-8.9 on Landrin persistence curves are shown in Figure 1 C and D; organic matter (O.M.) content was either 0.3% or 0.8%. It is clear that soil pH is basic in the breakdown of Landrin, as expected from the earlier data on alkaline hydrolysis. Persistence curves for Landrin in 3 soils with the same pH (7.9) but with different O.M. contents are shown in Figure 2. Although Landrin loss in

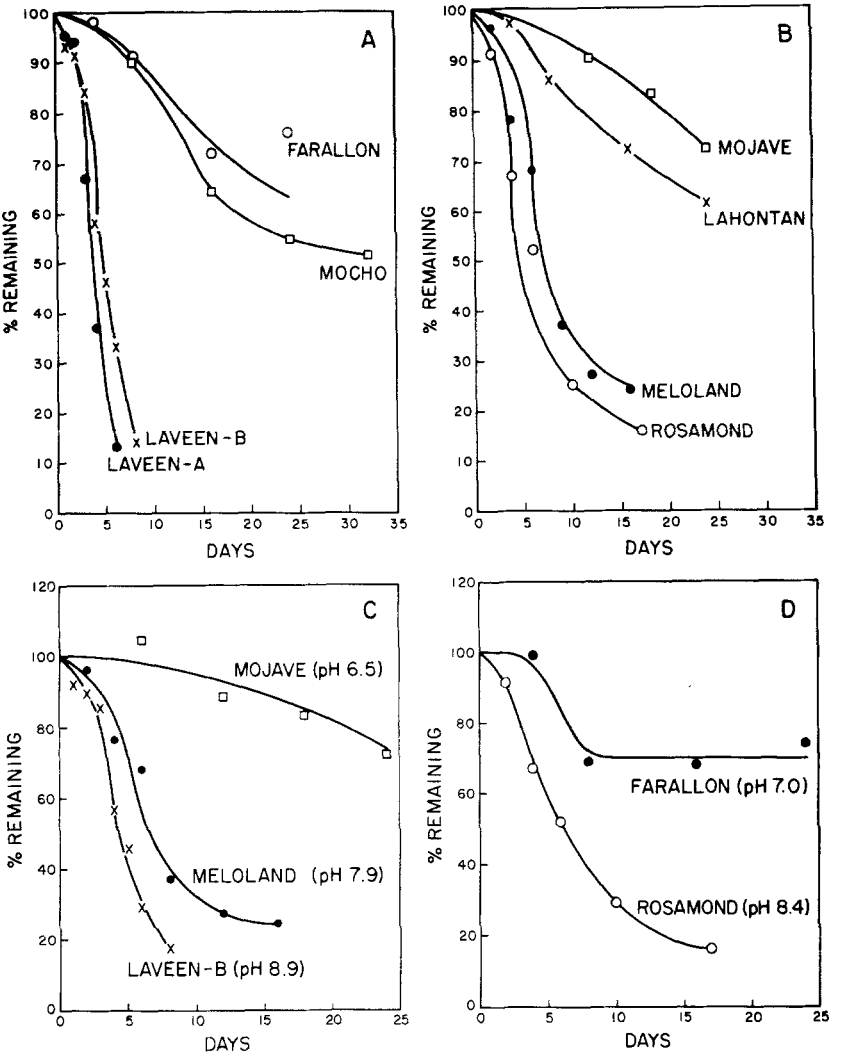

Figure 1. A and B show the persistence of Landrin in 8 diverse soil types at 37 ° C; see Table II for soil characteristics. The effect of soil pH on the persistence of Landrin is shown in soils with 0.3% organic matter (C) and with 0.8% organic matter (D).

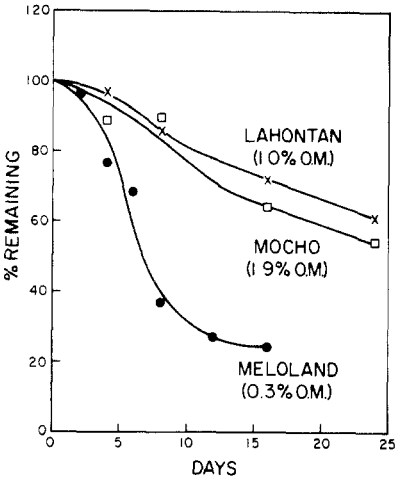

Figure 2. Effect of soil organic matter (O.M.) content on persistence of Landrin in soils of pH 7.9 at 37° C.

Meloland soil (0.3% O.M.) was most rapid, there was little difference between the other two (1.0 and 1.9% O.M.).

The shapes of these persistence curves indicate that losses of Landrin from these soils were due partially to the action of microorganisms: purely first- and second-order chemical breakdowns would not be expected to exhibit induction periods. On the other hand, for biological breakdown a time lag (observed here) during which the organisms were adjusting to the new substrate should be followed by an increasing rate of destruction (see KAUFMAN and KEARNEY 1970).

SUMMARY

The rates of dissipation of Landrin from nonsterile soils were primarily dependent upon the soil type. The persistence half-lives of the Landrin applied ranged from <4 to >40 days in the 8 soils investigated. Rates of breakdown increased with increasing soil pH (above pH 7), indicating alkaline hydrolysis as the major cause of Landrin degradation; destructive microorganisms were also involved, however. Soil organic matter did not seem to be a major factor in Landrin degradation.

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