Persistence of Permethrin and WL 43775 in Soil

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Six soils, fortified with permethrin or WL 43775 at 1 mg/kg, were incubated for 16 weeks at temperatures alternating between 20 °C for 15 h and 10 °C for 9 h. Initially and at 4-week intervals soils were sampled and analyzed. In five of the soils degradation of both insecticides was rapid, resulting in half-lives of approximately 3 weeks for *cis*- and *trans*-permethrin and 7 weeks for WL 43775. In the other soil very little degradation occurred: recovery after 16 weeks was greater than 75% for *cis*-permethrin and WL 43775, slightly less for *trans*-permethrin. Sterilization of two of the soils in which degradation was rapid greatly reduced the rate, indicating that microbial degradation was the chief factor in loss of these insecticides.

Permethrin [3-phenoxybenzyl (±)-*cis,trans*-3-(2,2-dichlorovinyl-2,2-dimethylcyclopropanecarboxylate] (NRDC 143, FMC33297) and WL 43775 [α-cyano-3-phenoxybenzyl-2-(4-chlorophenyl)-3-methyl-1-butyrate] are two of the newer synthetic pyrethroid insecticides being evaluated at this laboratory as possible control agents for tuber flea beetle (*Epitrix tuberis* Gent.) on potatoes and lepidoptera on crucifers.

As part of this evaluation it was desirable to examine persistence of these insecticides in a variety of soils. The purpose was twofold: to determine their persistence in soil as residues from spray applications and to examine the possibility of their use as soil insecticides in certain soils.

In a recent study of permethrin degradation in soil Kaufman et al. (1977) working with ^{14}C-labeled material found that, in four of the five soils tested, degradation of permethrin was rapid. Half-lives averaged 28 days or less. No other references to soil degradation of this insecticide or WL 43775 were found in the literature.

EXPERIMENTAL SECTION

Materials. Fresh soils from six agricultural regions of British Columbia were used in these experiments. Their location, physical properties, and pH are listed in Table I. Before use, soils were dried at room temperature until they could be screened through a 10-mesh sieve. The soil moisture at this stage was about 20–25%. Permethrin (40:60 cis/trans) and the pure cis and trans isomers were supplied by FMC Corp., Middleport, N.Y.; WL 43775 (98.5% purity) was supplied by Shell Research Ltd., Sittingbourne, U.K. Standard solutions of each were prepared containing 100 μg/mL in benzene. Solvents were pesticide grade or freshly redistilled reagent grade.

Soil Fortification. Soil was fortified with permethrin (mixed isomers) or WL 43775 at 1 mg/kg by adding the appropriate volume of standard solution to 10% of the total sample being fortified and, after evaporating the solvent, adding this portion to the remainder of the sample. The fortified soil, in a screw-capped jar, was tumbled in a Fisher-Kendall mixer for 2 h, then sampled and analyzed. Its moisture content was also determined.

Incubation. Duplicate 150-g portions of each fortified soil were transferred to 7.5-cm pots standing in petri dishes. Water was added to the petri dishes in small amounts until the soil surface was uniformly damp. The pots were covered and transferred to an unlighted environmental chamber in which the temperature was alternated between 20 °C for 15 h and 10 °C for 9 h (average day and night summer temperature). Moisture content of the soils was maintained at approximately the same level throughout the experiment. At intervals of 4, 8, 12, and 16 weeks, 25-g samples were removed from each pot for analysis. Smaller samples, in duplicate, were taken at the same time for moisture determination.

Soil Sterilization. Two soil samples, Abbotsford and Dawson Creek, were sterilized by autoclaving for 1 h at 121 °C and 15 psi on two successive days. These, and corresponding nonsterile samples, were fortified, incubated, and sampled at intervals of 0, 2, 4, and 6 weeks as described above. Samples fortified wih WL43775 were also sampled at 8 weeks.

Analytical Procedure. *Extraction.* A 25-g soil sample was extracted with 50 mL of 1:1 v/v hexane/acetone by shaking for 30 min in a 250-mL glass-stoppered Erlenmeyer flask. The supernatant solvent was decanted through a glass-filter-lined Büchner funnel into a 1-L separatory funnel. Extraction was repeated twice more. The combined filtrates plus 600 mL of water and 10 mL of a saturated aqueous solution of sodium chloride were well shaken. The two phases were allowed to separate, and the aqueous phase was drawn off into a second 1-L separatory funnel, reextracted with 25 mL of hexane, then discarded. The combined hexane extracts were washed with 100 mL of water plus 5 mL of saturated sodium chloride solution, dried by filtering through anhydrous sodium sulfate, and evaporated to near dryness on a rotary vacuum evaporator. The residue was transferred quantitatively to a 25-mL volumetric flask and diluted to volume with hexane washings.

Cleanup. A micro cleanup column consisting of a Pasteur pipet packed with mixed adsorbents has been previously described (Williams, 1976). After prewashing this column with 3 mL of hexane, a 1-mL aliquot of the soil extract was allowed to drain through it. The column was washed with 3 mL of hexane, then permethrin or WL 43775 was eluted with 7 mL of benzene. The eluate was collected in a 10-mL Kuderna Danish concentrating tube, evaporated to near dryness under a stream of air in a fume hood, then diluted to exactly 1 mL. The sample was then ready for GC analysis.

Gas Chromatographic Analysis. A Tracor Model MT 220 gas chromatograph fitted with a ^{63}Ni electron-capture detector was used for analysis. For permethrin, the column was 180 cm × 2 mm i.d. glass, packed with 3% SP 2330 (Supelco Inc. Bellefonte, Pa.) on 60–80 mesh Gas-Chrom Q. Flow rate of the nitrogen carrier gas was 65 mL/min, and column temperature was 220 °C, inlet temperature 230 °C, and detector temperature 275 °C. Under these conditions a complete separation of the two isomers of permethrin was achieved. For WL 43775, the column was 45 cm × 2 mm i.d. glass, packed with 3% OV-3 on 60–80 mesh Gas-Chrom Q. Inlet and detector temperatures were as for permethrin but carrier gas flow was 75 mL/min and

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Table I. Some Physical Properties and pH of Six British Columbia Soils

location	constituents (% dry weight) organic matter	sand	silt	clay	moisture, % (air-dried sample)	pH	type
Abbotsford	5.1	37.5	51.3	6.1	3.2	5.76	silt loam
Cloverdale	51.8	6.5	32.1	9.6	15.7	4.06	organic
Dawson Creek	8.5	24.5	42.2	24.8	3.7	6.03	clay loam
Penticton	3.0	21.7	65.1	10.9	7.9	7.90	silt loam
Prince George	5.1	11.0	69.1	14.8	3.2	6.56	silt loam
Kamloops	5.4	2.6	57.7	34.2	3.1	6.02	silty clay loam

Table II. Recovery of Permethrin (40:60 cis/trans) and WL 43775 from Sterile and Nonsterile Soils

soil sample	period weeks	recovery, ppm *cis*-permethrin sterile	*cis*-permethrin nonsterile	*trans*-permethrin sterile	*trans*-permethrin nonsterile	WL 43775 sterile	WL 43775 nonsterile
Abbotsford	0	0.38	0.37	0.56	0.60	0.99	0.95
	2	0.30	0.18	0.54	0.19	0.69	0.78
	4	0.22	0.09	0.44	0.10	0.91	0.67
	6	0.28	0.09	0.50	0.07	0.88	0.56
	8					0.86	0.45
Dawson Creek	0	0.42	0.42	0.65	0.64	1.02	1.00
	2	0.32	0.37	0.62	0.47	0.74	0.84
	4	0.30	0.17	0.49	0.14	1.05	0.96
	6	0.36	0.12	0.64	0.11	0.83	0.56
	8					1.02	0.47

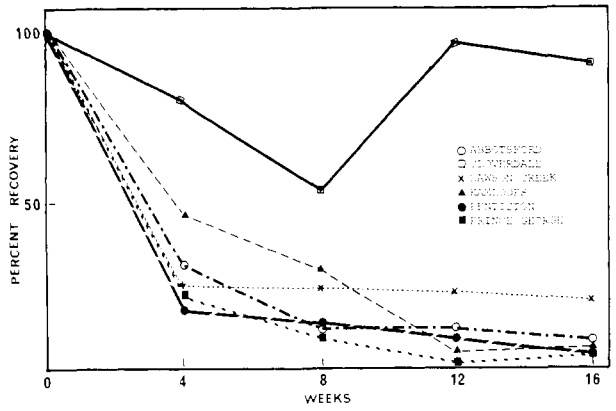

Figure 1. Loss of *cis*-permethrin from six soils over a 16-week period.

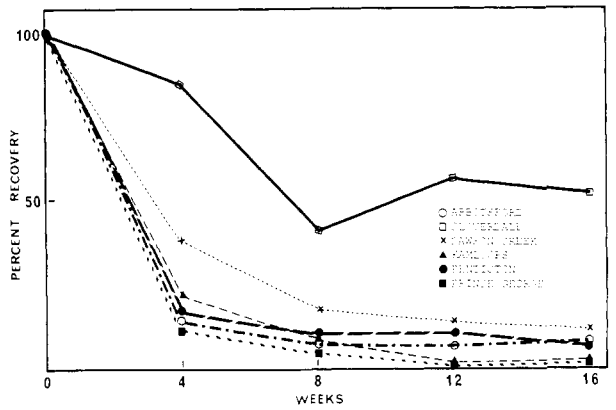

Figure 2. Loss of *trans*-permethrin from six soils over a 16-week period.

column temperature was 225 °C. Samples of 5 μL were injected and quantitation was by comparison of peak heights with a series of appropriate standards. Results were calculated on a dry weight basis.

RESULTS AND DISCUSSION

Degradation of *cis*-permethrin is shown in Figure 1, of *trans*-permethrin in Figure 2, and of WL 43775 in Figure 3. Points plotted indicate percent recovery of the amounts originally present. Each is the average of two replicates which generally differed by less than 10%. There are a few unexplained discrepancies, for example, the lower recovery of permethrin in Cloverdale soil at 8 weeks than at 12 weeks. Degradation of both permethrin and WL 43775 was slow in the soil from Cloverdale, with little loss of either insecticide over 16 weeks. With the exception of the Cloverdale sample, degradation of both insecticides was rapid in all soils. In these soils half-lives for both isomers of permethrin were 3 weeks or less, while for WL 43775 half-lives were approximately 7 weeks. In the soils in which degradation was rapid, loss of *trans*-permethrin was significantly greater than that of *cis*-permethrin, while in the Cloverdale soil, losses were similar.

The effect of soil sterilization on the degradation of the insecticides is shown in Table II. Losses from sterile and nonsterile soils are compared over a period of 6 weeks for

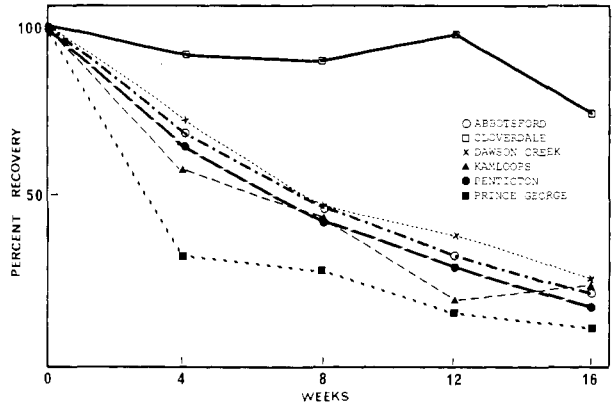

Figure 3. Loss of WL 43775 from six soils over a 16-week period.

permethrin and 8 weeks for WL 43775. The two soils chosen for this experiment were from Abbotsford and Dawson Creek. Both had a similar and relatively high pH but differed in physical properties, the Abbotsford soil being a silt loam and the Dawson Creek soil a clay loam.

Over the test period there was very little loss of either insecticide in the sterilized soils, while in the nonsterile soils losses were essentially the same as previously found. Although the sterilized soils were not strictly sterile by the

time they had been transferred to pots and moistened with water, the results clearly demonstrate that microbial activity is the major factor in the loss of these insecticides.

The degradation rates in the Cloverdale soil are obviously quite different from the general pattern shown by the other soils. The pH of the Cloverdale soil was significantly lower than that of all other soils and may possibly have affected the degradation rate. The Cloverdale soil was also the only organic soil in the experiment and adsorption onto the larger organic fraction may have contributed significantly to the decreased degradation rate.

LITERATURE CITED

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Quantitative Thin-Layer Chromatographic Determination of Br^- Residues in Crops after Soil Treatment by Methyl Bromide

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A procedure is described for the quantitative thin-layer chromatographic determination of Br^- residues in crops grown on soils treated with methyl bromide. The samples are dried and calcinated. The ashes are extracted with water. The Br^- containing solution is spotted on a heated silica gel coated chromatographic plate. The plate is covered with a glass plate just above the spots, sprayed successively with a fluorescein solution and a mixture of glacial HOAc and 30% H_2O_2. After heating, Br^- reacts with fluorescein to form eosin. Bright red spots appear on a yellow background. This reaction is specific for Br^-. After development of the plate, fluorescein, eosin, and small amounts of other brominated products of fluorescein are distinctly separated. The eosin spots are marked and scraped off. The eosin is eluted from the silica gel with distilled water and measured spectrophotometrically at 521 nm. The calibration curve is linear from 10 to 90 ppm Br^-. The results obtained by this method are compared with an X-ray fluorescence spectroscopic technique.

Intensive crop cultures, especially in greenhouses, require a careful control of the soil conditions. Furthermore, to obtain good yields in those cultures it is necessary to eliminate harmful effects of weeds, mold, and eelworms as much as possible. Therefore, the treatment with pesticides, fungicides, and soil disinfectants is practically unavoidable. Their use, however, may give rise to new problems, such as those related to the presence of their residues in the plant.

Among the many soil disinfectants methyl bromide takes an important place because of its efficacy. After application, CH_3Br is rapidly converted to inorganic bromide in the soil and can be accumulated by the plant in that form. Apart from the aspect of public health related to the presence of the bromide, it can also cause phytotoxic action.

For assessing the bromide residues in plant material, there are several methods of analysis. A method based on "neutron activation analysis" has been described by Guinn and Potter (1962), Castro and Schmitt (1962), and Stärk et al. (1971). A promising technique proves to be X-ray fluorescence spectroscopy (Van Cauwenberge and Gordts, 1977). A colorimetric procedure has been developed by Drosihn (1967) and Malkomes (1970) and is based on calcination of the plant material and oxidation of bromide to hypobromite, which reacts, in a buffered medium, with phenol red to form tetrabromophenol blue. A gas chromatographic technique has been proposed by Heuser and Scudamore (1970). In this method the inorganic bromide reacts with ethylene oxide in diisopropyl ether to form 2-bromoethanol which can be determined by gas chromatography.

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However, these methods suffer from certain disadvantages. The first two require a special and costly instrumentation while the third and the fourth techniques are rather cumbersome and time consuming.

In this work it was our purpose to evaluate the possibilities of a technique which is fairly rapid, specific, and easily applicable, by simple means, in the laboratories dealing frequently with pesticide residue analysis. We thought that calcination, separation of the halides with thin-layer chromatography, and, after scraping of the spots, spectrophotometric determination might offer a solution. Separating techniques are described by Gagliardi and Likussar (1965) and Berger et al. (1964). The separation of Br^- was good but the methods proved inadequate for further quantitative work. Feigl (1954) showed that the bromination of fluorescein made a very sensitive and specific spot test. Axelrod et al. (1971) took this as a basis for the fluorimetric determination of bromine in aerosols.

We successfully tried the separation of halides on TLC silica gel plates with fluorescein and glacial HOAc–H_2O_2 as visualizing reagents. After development of the plates they were sprayed with an alcoholic solution of sodium fluorescein immediately followed by spraying with a freshly prepared mixture of glacial HOAc–30% H_2O_2 (50:50). After heating for 5 min at 110 °C, a well-defined red spot of tetrabromofluorescein (eosin) appears on a yellow background. Three bromo-substituted products of fluorescein are also visible with minor intensity. The other halides are not revealed.

Again the background intensity did not allow the quantitative determination. To eliminate this disturbance the color formation was carried out before the separation. For this purpose the TLC plate is covered with a glass plate just above the spots, sprayed with the reagents, heated, and developed. Solvents for the separation of fluorescein and eosin are proposed by Naff and Naff (1963)

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