Effect of Pesticide Formulation on the Distribution of Fenitrothion on Apple Foliage

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The distribution of fenitrothion on apple foliage was determined in the spring of successive years, with a different commercial formulation in each year. The surface deposits and residues were removed with three 30-s rinses with a chloroform–methanol solvent, and the subsurface residues were extracted by homogenizing with more of the same solvent. Following a silica gel purification, fenitrothion was determined by gas chromatography with flame photometric detection. In the first year, for three successive spray applications, the percentages of fenitrothion found in the subsurface extract relative to the total deposit on the day of application were 18.5, 18.4, and 16.9, respectively. In the following year for two successive spray applications the percentages were 34.4 and 37.0, respectively. This large but consistent difference in fenitrothion distribution appears to have resulted from a change in formulation of fenitrothion since climatic conditions and stages of foliage development were similar in both years.

Fenitrothion, O,O-dimethyl O-(3-methyl-4-nitrophenyl) phosphorothiate, a systemic contact insecticide, was used for the control of several insect pests and overwintering larvae. The persistance and distribution of fenitrothion spray deposits and residues on apple foliage were determined in successive years in order to evaluate the residual effectiveness of this insecticide under field conditions. The technique in removal of surface cuticular spray deposits and residues was based on the previous work of Martin (1960), Robers et al. (1961), Eglinton et al. (1962), and Silva Fernandes et al. (1964), on isolation and characterization of apple cuticular waxes using chloroform as the solvent. In the present investigation, a chloroform–methanol (9:1 v/v) solvent was used instead of chloroform and was found to be equally effective in cuticular wax removal. The method of analysis used was developed by Bowman and Beroza (1969) and subsequently used for Leuck and Bowman (1969) for fenitrothion residue analysis.

MATERIALS AND METHODS

Spray Applications. A row of 24 8-year-old Cox's Orange Pippin apple trees was used for the investigation. All pesticides were applied to run off as aqueous emulsions by a conventional medium-volume mist blower. Details of stages of apple foliage development and application rates of fenitrothion are given in Table I. Fungicides applied together with fenitrothion are also given.

Sampling. All samples were taken randomly from all 24 trees at upper, middle, and lower levels. The gross samples were then subsampled in duplicate for analysis. Following each spray application, a period of 2–3 h was allowed to elapse before sampling to allow the spray deposits to dry out. Subsequent samples were taken at selected daily intervals. All samples were processed within 3 h of collection.

Materials, Equipment, and Method of Analysis. *Chemicals.* Solvents were as follows: chloroform, methanol, acetone, and benzene. All solvents were glass distilled before used. The adsorbent used was MN Kieselgel (Machery-Nagel and Co., 35–70 mesh). The moisture content of each batch of adsorbent was found by heating

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Table I. Spray Applications of Fenitrothion

application date	stage of foliage development	application rate, kg/ha	other pesticides applied
First Year: Formulation Used Was Accothion (Cyanamid) 50% e.c.			
April 1	mouse ear	0.23	dodine
April 23	green cluster	0.11	dodine
May 1	pink bud	0.23	captan
Second Year: Formulation Used Was Fentro-50 (Murphy) 50% e.c.			
April 23	green cluster	0.09	dodine
May 4	pink bud	0.06	captan

portions at 130 °C for 12 h and reweighing. The remaining material was deactivated in 200-g batches by adding the appropriate amount of water to provide a 20% moisture content and shaking for 4 h before use. Sodium sulfate was anhydrous, analytical grade and heated at 550 °C for 12 h and cooled in a desiccator. The fenitrothion standard was of 98% purity and supplied by Bayer Leverkusen, West Germany.

Equipment. The gas chromatograph was a Varian aerograph, dual-channel moduline series 2700, equipped with a Tracor flame photometric detector. The recorder was W and W Model 1200. The homogenizer used was an MSE homogenizer (MSE Scientific Instruments, West Sussex, England). The gas chromatographic column was as follows: 1.5 m × 3 mm i.d. glass column, packed with 4% SE-30 coated on 60–80-mesh Gas-Chrom Q; conditioned at 240 °C for 12 h with nitrogen carrier gas at a flow rate of 60 mL/min. The operating conditions were as follows: temperature (°C), injector 250, column 235, and detector 290; nitrogen flow rate, 60 mL/min. Under these conditions, the retention time of fenitrothion was 2.0 min. The column was preconditioned to fenitrothion by injection of 3 × 2 μg amounts of the insecticide into the column under operating conditions just prior to analyses. Further injections of 10-ng quantities were then made until a reproducible response was obtained. The column was then considered ready for use. The flame photometric detector operating conditions were as follows. The detector was operated in the phosphorus-detecting mode with optimized gas flow rates as follows (mL/min): hydrogen, 200; oxygen, 20; air, 100.

Extraction. Chloroform–methanol (9:1 v/v) solvent was used instead of chloroform since it was found to be more

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effective than chloroform in the extraction of fenitrothion and other pesticides used in the plant protection program. The efficiency of the two solvents in surface cuticular wax removal was compared and found to be similar. The weights of cuticular wax removed per gram of apple foliage were not significantly different ($p < 0.05$), and the thin-layer chromatograms of the respective extracts were similar.

Subsamples of treated foliage (10 g) were placed in 100-mL MSE vortex beakers and given three consecutive 30-s rinses with 30-mL aliquots of chloroform–methanol (9:1 v/v) solvent at room temperature to remove the surface pesticide deposits. The foliage was then homogenized with 50 mL more solvent and 15 g of anhydrous sodium sulfate at high speed for 2 min to extract the remaining fenitrothion. Each sample extract was percolated through 20 g of anhydrous sodium sulfate held on a G2 porosity sinter in cylindrical funnels (18 × 4 cm) under slight water pump vacuum. A further 50 mL of solvent was used to rinse each flask and residue, and the combined extract was evaporated to dryness on a rotary evaporator at water bath temperature of 50 °C. The residual solvent was removed with a gentle stream of air, and the extract was redissolved in small amounts of benzene for liquid column chromatographic purification.

Liquid Chromatographic Purification. The procedure used was as described by Bowman and Beroza (1969).

RESULTS AND DISCUSSION

Fenitrothion that was extracted together with the cuticular waxes is regarded as the surface cuticular deposit or residue. Likewise, the remaining fenitrothion extracted by maceration of the foliage is described as the subsurface fraction. The distribution of fenitrothion is given in Table II. All values are given as mean concentrations ± percentage deviations about the mean. The day to day distribution of the subsurface residues relative to the total fenitrothion concentration is given in the final column.

From the results in Table II it is evident that the initial distribution of fenitrothion on apple foliage on the days of application was very consistent in the respective years. In the first year the values of percentage subsurface fenitrothion found relative to the total deposit were 18.5, 18.4, and 16.9% (mean 17.9%). In the following year the corresponding values were 34.4 and 37.0% (mean 35.7%) in spite of different dosages applied on each occasion. Carry-over of fenitrothion residues from one application to another is considered negligible (1% or less of the following day 0 values), except possibly between the second and third applications in the first year. On the latter occasion the residues on the day prior to the third application were 8.1% of the subsurface value obtained following that application. However, the actual residual value is expected to be significantly lower in view of the rapid rate of disappearance of fenitrothion experienced. In both years the ambient temperature averaged about 5 °C and sunshine duration about 5 h daily, with very little rainfall (<2 mm) on the days of application. Under the circumstances the difference in fenitrothion distribution was best explained by the change in formulation used since the same trees at similar periods of foliage development were used.

Surfactants have been shown to facilitate the uptake of other compounds into foliage (Bayer and Lumb, 1973; Holly, 1976) as well as enter the plants themselves (Price, 1977) and thus affect the distribution of foliarly applied chemicals. On the other hand, some surfactants reduce

Table II. Fenitrothion Distribution on Apple Foliage

days following spray	fenitrothion concentration		
	surface, ng/g	subsurface, ng/g	% subsurface/ total
First Year			
0 (application date April 1)	12270 ± 9.9	2780 ± 9.4	18.5
1	793 ± 7.1	637 ± 5.8	44.5
3	366 ± 3.8	125 ± 4.0	25.5
6	39 ± 5.1	97 ± 7.2	71.3
17	15 ± 0.0	30 ± 3.3	66.7
0 (application date April 23)	21389 ± 12.4	4810 ± 8.5	18.4
1	11120 ± 9.8	1820 ± 6.6	14.1
2	2350 ± 6.4	2230 ± 3.6	53.5
5	425 ± 5.9	270 ± 3.7	38.8
7	350 ± 3.4	210 ± 7.1	37.5
0 (application date May 1)	12750 ± 10.1	2600 ± 9.6	16.9
1	6800 ± 6.6	2060 ± 7.8	23.3
2	3400 ± 6.8	2350 ± 2.1	40.9
6	600 ± 3.3	438 ± 2.7	42.2
29	20 ± 2.0	14 ± 2.5	41.2
Second Year			
0 (application date April 23)	11250 ± 11.1	5900 ± 11.1	34.4
1	3050 ± 5.9	3800 ± 7.9	55.5
3	1500 ± 7.3	1080 ± 2.8	41.9
6	175 ± 5.7	175 ± 2.8	50.0
11	80 ± 8.0	75 ± 5.0	48.4
0 (application date May 4)	8000 ± 12.5	4700 ± 9.6	37.0
1	4700 ± 7.0	4300 ± 7.0	47.8
3	2050 ± 12.2	1550 ± 3.2	43.1
	75 ± 9.3	410 ± 4.9	84.5

the penetration of organic compounds on foliage (Goodman, 1962), and the concentration of surfactant in a formulation is important in this respect (Jansen, 1961). Although the nature and concentration of the surfactants used in the two commercial formulations used were not investigated, owing to the large number of surfactants in normal use (Becher, 1973), the likelihood of their being different is quite strong.

Following the application of fenitrothion, it is also apparent that in time the ratio of subsurface to surface cuticular residues increased in both years. Such distributions did not appear to be correlated with rainfall, sunshine duration, or ambient temperatures over the periods investigated. Rather, it is suggested that continued penetration and translocation of the insecticide consistent with its systemic nature, coupled with losses by volatilization, weathering by rainfall, or photochemical degradation, which has been shown to occur readily (Ohkawa et al., 1974), were responsible for the later distribution pattern of the insecticide. This suggestion is supported by the nonlinearity of first- and second-order kinetic plots of total fenitrothion vs. time.

The commercial formulation used in the second year (Fentro-50) shows better potential systemic activity than that (Accothion) used in the first year. In the context of the present study, however, since the insecticide, described as a contact insecticide, was applied against surface feeding pests, then much of its contact activity would have been lost by subcuticular penetration and translocation unless it subsequently reissued to the surface. In view of the low persistence of the insecticide under field conditions, the protective cover provided by the spray application therefore appears to be dependent on the formulation used.

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New Perspectives on the Hydrolytic Degradation of the Organophosphorothioate Insecticide Chlorpyrifos

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The disappearance kinetics in water for chlorpyrifos [O,O-diethyl O-(3,5,6-trichloro-2-pyridyl) phosphorothioate], an important insecticide, has been investigated to provide a kinetic expression to define the hydrolysis process in aquatic ecosystems. Pseudo-first-order kinetics are observed over the pH range of 1–13. The rate constant is independent of pH from pH 1 to pH 7 and has a value of $(6.2 \pm 0.9) \times 10^{-6}$ min^{-1} at 25 °C. At alkaline pHs, the rate constant is much larger but is not directly proportional to hydroxide activity. The observed behavior over the pH range 10–12 is consistent, however, with equilibrium formation of a 5-coordinate charged hydroxyphosphorothioate intermediate and the rate-controlling decomposition of this intermediate to products. Thus, the second-order rate expression does not accurately describe the kinetics of degradation at alkaline pHs. Product studies over the alkaline pH range (9–13) show that the only major products are 3,5,6-trichloro-2-pyridinol and O,O-diethyl phosphorothioic acid.

Organophosphorothioates comprise a large and important class of compounds in use as environmental chemicals ("Farm Chemicals Handbook", 1981). Because these compounds may appear in environmental waters, efforts have been made to describe the chemical reactions that these compounds undergo in aquatic ecosystems (Wolfe et al., 1978; Paris et al., 1981). In particular, recent hydrolysis and biolysis studies have focused on the development of quantitative expressions for use in models to forecast the fate of such pollutants in aquatic ecosystems. These usually detailed studies are aimed at obtaining the disappearance rate constants in either first-order or second-order rate expressions.

Detailed knowledge of the kinetics of the alkaline and neutral hydrolysis pathways is critical to several areas of environmental chemistry. Such knowledge is particularly pertinent in designing experiments to obtain reliable rate constants for use in assessing the fate and transport of

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pollutants in aquatic ecosystems. Another example is the development of structure reactivity relationships for use in predicting alkaline or neutral hydrolysis rate constants of organophosphate and phosphorothioate esters (Wolfe, 1980). The correlation between alkaline hydrolysis and some physiochemical property of the congeners (e.g., pK_a of the leaving group) requires a data base of alkaline hydrolysis rate constants. Even more fundamental is an understanding of the microbial degradation process and the relationship between enzymatic hydrolysis and abiotic hydrolysis (Wolfe et al., 1980). Such relationships have been reported for other classes of compounds and have potential in elucidating the degradative pathways of phosphorothioate esters in the aquatic environment.

Chlorpyrifos, a model compound representative of the organophosphorothioate insecticides, was studied in aquatic ecosystems because of its potential to hydrolyze not only in the water column but also in the bottom sediments. It is generally accepted that the alkaline hydrolysis of organophosphorus esters is described by a second-order rate expression that is first order in ester and first order in hydroxide ion activities (Cox and Ramsay, 1964). Thus, a plot of log observed rate constant vs. pH for the alkaline hydrolysis should be linear with a slope of 1. In the case of chlorpyrifos, however, such a plot is nonlinear. Fur-